QUATORZIÈME COLLOQUE SUR LA SPECTROSCOPIE MOLÉCULAIRE À HAUTE RÉSOLUTION

FOURTEENTH COLLOQUIUM ON HIGH RESOLUTION MOLECULAR SPECTROSCOPY

ACTES DU COLLOQUE INTERNATIONAL DE DIJON
11 - 15 SEPTEMBRE 1995

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Universite Pierre et Marie Curie et C.N.R.S.
3 rue Michel-Ange
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Coherent's Laser Products

Continuous Wave Lasers

- **Ion**

IR	752nm	— 1090nm
Visible	407nm	— 676nm
UV	300nm	— 386nm
DUV	229nm	— 284nm

- **Diode-Pumped Solid-State**

IR	1064nm
Visible	532nm

- **Tunable Ti:S/Dye**

IR	750nm	— 1080nm
Visible	400nm	— 750nm
UV	225nm	— 400nm

- **Nd:YAG/Nd:YLF**

IR	1064nm/1053nm

- **CO_2**

IR	10.6μm/11.4μm

Nanosecond Pulsed Lasers

- **Nd:YAG**

IR	1064nm
SHG	532nm
THG	355nm
FHG	266nm

Modelocked Lasers

- **Femtosecond Ti:S/Dye**

IR	750nm	— 1060nm
Visible	400nm	— 750nm
UV	240nm	— 400nm

- **Femtosecond OPA**

IR	900nm	— 2500nm
Visible	450nm	— 700nm

- **Picosecond Ti:S/Dye**

IR	700nm	— 1060nm
Visible	400nm	— 750nm
UV	240nm	— 400nm

- **Picosecond Nd:YAG/Nd:YLF**

IR	1064nm/1053nm
Visible	532nm/527nm
UV	355nm/351nm

- **Picosecond Ion**

Visible	458nm	— 515nm

Typical Laser Applications

Scientific Research
- Spectroscopy
- Nonlinear Optics
- Interferometry

Instrumentation
- Inspection
- Biotechnology
- Flow Visualization

Manufacturing
- Materials Processing
- Materials Research
- Materials Inspection

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Laser Entertainment
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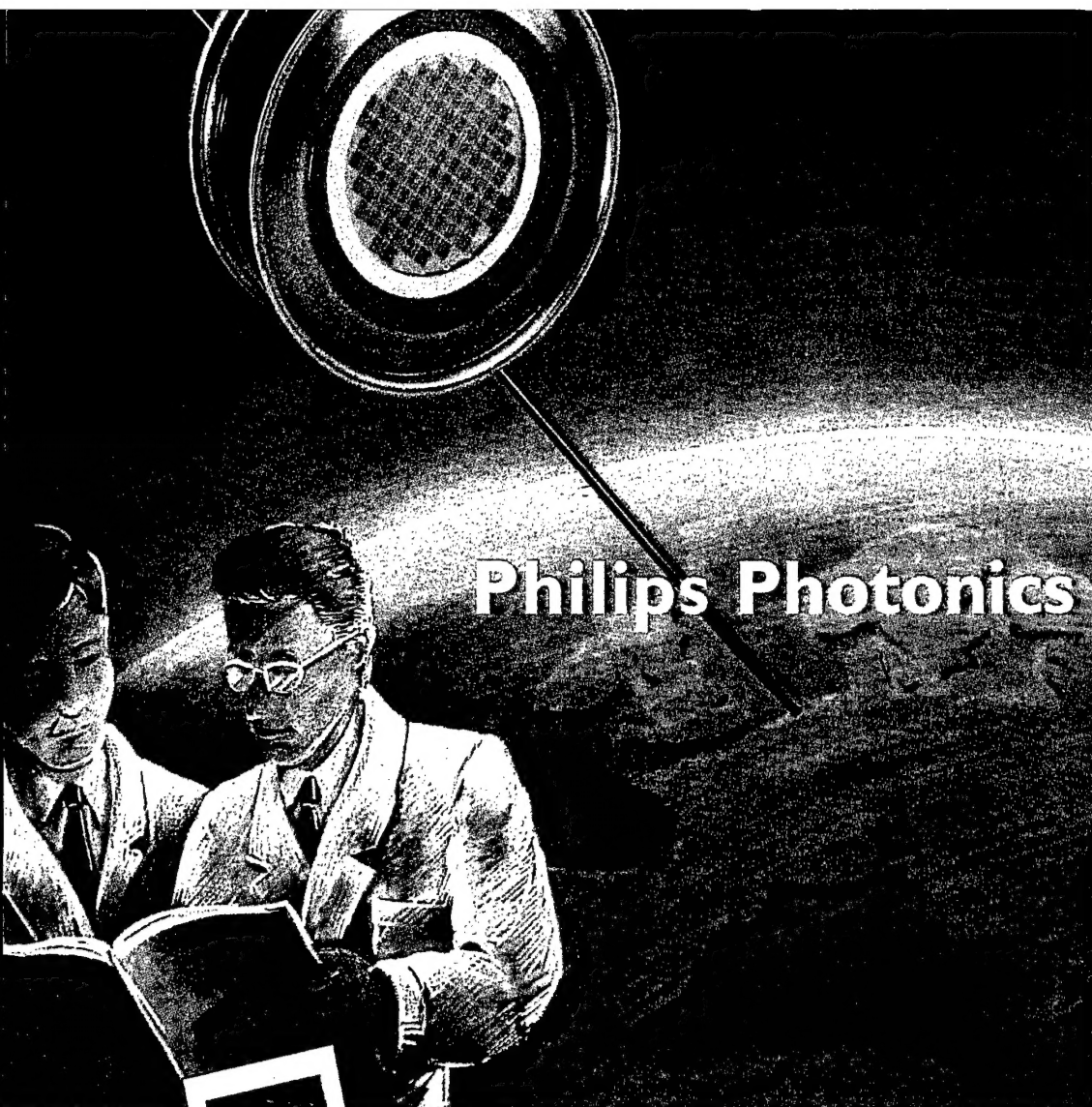- Graphic Displays
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- Research
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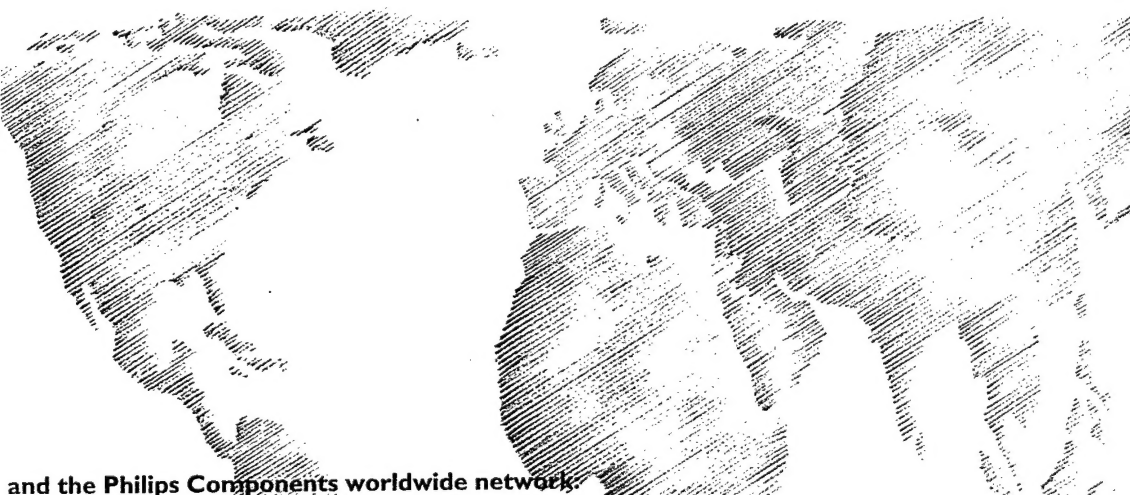Tel: +33 1-40996069
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Bulgaria
Tel: +32 2-6758610
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China (PR)
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CIS
Tel: +31 40-723217
Fax: +31 40-723085

Czechia & Slovakia
Tel: +49 40-3296640
Fax: +49 40-3296917

Denmark
Tel: +(0)86-848484
Fax: +(0)86-848244

Finland
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Greece
Tel: (0)1-4894911
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Le COMITÉ LOCAL SOUHAITE REMERCIER LES PERSONNES DU LABORATOIRE AYANT PARTICIPÉ A L'ORGANISATION.

The Local Committee wishes to thank members of the laboratory, that have contributed to the Organization

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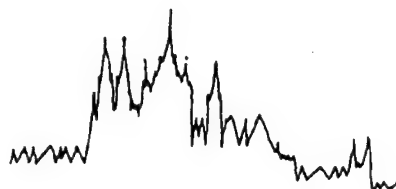
PRAHA96

The 14th International Conference on High Resolution Molecular Spectroscopy
Prague, Czech Republic, September 9-13, 1996

LOCAL ORGANIZING COMMITTEE

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The meeting is jointly organized by the J. Heyrovský Institute of Physical Chemistry in the Academy of Sciences of the Czech Republic, Prague, and by the Ioannes Marcus Marci Spectroscopical Society. The subjects covered are largely identical to those covered at the Fourteenth Colloquium on High Resolution Molecular Spectroscopy.

Information is available from the chairman of the local organizing committee,

Dr. Vladimír Špirko
Academy of Sciences of the Czech Republic
J. Heyrovský Institute of Physical Chemistry
Dolejškova 3, CZ-18223 Praha 8, Czech Republic.
Fax: +42 2 858 2307
E-mail: praha96@jh-inst.cas.cz
        praha96@wcpj.chemie.uni-wuppertal.de

The conference has a home page on the World Wide Web with URL

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This page will be used to provide up-to-date information. It also gives access to a fill-out-form which can be used to request the first circular.

DIJON - FRANCE

11 - 15 SEPTEMBRE 1995 - *SEPTEMBER 11 - 15th, 1995*

PROGRAMME DU COLLOQUE
PROGRAM OF THE COLLOQUIUM

DATES	11/09/95	12/09/95	13/09/95	14/09/95	15/09/95
Heures/Hours	LUNDI MONDAY	MARDI TUESDAY	MERCREDI WEDNESDAY	JEUDI THURSDAY	VENDREDI FRIDAY
9 H 00	INV.Speakers **A**	INV.Speakers **E**	INV.Speakers **J**	INV.Speakers **L**	INV.Speakers **P**
	+	+	+	+	+
10H30-12H30	POSTERS Sess. **B**	POSTERS Sess. **F**	POSTERS Sess. **K**	POSTERS Sess. **M**	POSTERS Sess. **Q**
12H30 - 14H00	Repas/Lunch	Repas/Lunch	Repas/Lunch	Repas/Lunch	Repas/Lunch
14 H 00	INV.Speakers **C**	INV.Speakers **G**	**Visite Touristique**	**LIBRE**	INV.Speakers **R**
	+	+			
16 H-18 H 00	POSTERS Sess. **D**	POSTERS Sess. **H**	Sight Seeing Tour	**FREE**	
19H00	Repas/Dinner			Repas/Dinner	
20 H 00		**TOWN HALL RECEPTION**	**BANQUET**	POSTERS Sess. **N**	

FOURTEENTH COLLOQUIUM
ON HIGH RESOLUTION
MOLECULAR SPECTROSCOPY

Dijon, September 11–15, 1995

PROGRAM OF SESSIONS

June 1995

MONDAY, SEPTEMBER 11   9:00

INVITED LECTURES
A

A 1 Frequency Measurements of Fluorescence-Stabilized CO_2 and N_2O Lasers : Accurate Molecular Constants and Frequencies
K. EVENSON

A 2 Intermolecular vibrations of aromatic molecule van der Waals complexes : exact quantum theory and experiment
S. LEUTWYLER

MONDAY, SEPTEMBER 11   10:30 – 12:30

POSTER SESSION
B

B 1 Lineshape parameters and Q branch shapes for absorption spectra of CH_3F in rare gases
I.M. GRIGORIEV, R. LE DOUCEN, A. BENIDAR, N.N. FILIPPOV, AND M.V. TONKOV

B 2 The potential Barrier of the $B^1\Pi_U$ State of Li_2
I. RUSSIER, F. MARTIN, A.J. ROSS, C. LINTON, P. CROZET, S. CHURASSY, AND R. BACIS

B 3 Extended Molecular Symmetry Groups for Systems with two coaxial Rotors
P. SOLDAN

B 4 Rovibrational Spectroscopy and Intramolecular Dynamics of Acetylene in the Electronic ground State
M. ABBOUTI TEMSAMANI AND M. HERMAN

B 5 Coherent Ion Dip spectroscopy of high lying vibrational states in the S_O potential surface of weakly bound molecular clusters
R. NEUHAUSER AND H.J. NEUSSER

B 6 The vibrational Energy pattern in Trans 1-2 Dichloroethane
Y. ELYOUSSOUFI, M. HERMAN, AND J. LIEVIN

B 7 $Na^7 Li 1^1 \Pi(B)$ Electronic State Λ-doubling Analysis
C.E. FELLOWS, R.F. GUTTERES, A. DIAS TAVARES JR., C. AMIOT, AND J. VERGÈS

B 8 High precision spectroscopy on I_2 in the near infrared
B. BODERMANN, H. KNÖCKEL, S. KREMSER, AND E. TIEMANN

B 23 High Resolution Study of the ν_2 Band of CH ^{35}Cl$_3$
V.M. HORNEMAN, R. PASO, J. PIETILÄ, AND R. ANTTILA

B 24 High Resolution Photoacoustic Spectrum of HCCBr
O. VAITTINEN AND L. HALONEN

B 25 Raman Intensities of ^{12}CD$_4$ in the Pentad Region
L. TOUZANI, M. LOËTE, B. LAVOREL, AND G. MILLOT

B 26 Prediction and Observation of the Stark Effect in the ν_3 band of SiF$_4$ - Transition
Intensities
M.P. COQUARD, M. LOËTE, A. AINETSCHIAN, AND W.A. KREINER

B 27 Algebraic approach to Vibrational Spectra of tetrahedral molecules. First order
infrared intensity model
C. LEROY, F. COLLIN, AND M. LOËTE

B 28 High Resolution Absorption Spectrum of Nitryl Chloride, ClNO$_2$ at 793cm^{-1}
G. DUXBURY AND R. McPHEAT

B 29 Simple Modeling of Q-Branch Absorption. Pressure, Temperature, and Perturber
Dependences in the $2\nu_6$ Q-Branch of ^{12}CH^{35}ClF$_2$
G. BLANQUET, J. WALRAND, J.M. HARTMANN, AND J.P. BOUANICH

B 30 A Software Package for Assignments of Vibration- Rotation Bands of Asymmetric
Top Molecules
S. URBAN AND J. BEHREND

B 31 The MM-Wave Rotational Spectrum of CBrClF$_2$
E. BIALKOWSKA, Z. KISIEL, AND L. PSZCZOLKOWSKI

B 32 High Resolution FTIR-Spectra of The Parallel Band ν_{12} of ^{13}C-Triazine
M. PFEFFER AND A RUOFF

B 33 Fourier Transform Spectrum and Morbid Calculations of Phosphaethyne (HCP)
M. JUNG, M. MENGEL, AND M. WINNEWISSER

B 34 The ν_{10} Bandof Propyne-d$_1$ with the resolution of 0.001 cm^{-1} using a Syn-
chrotron Radiation Source
R. PASO, V.M. HORNEMAN, R. ANTTILA, A.M. TOLONEN, AND S. ALANKO

B 35 FT-Microwave Spectrum, Large-Amplitude Motions, and ab initio Calculations
for N$_2$O$_5$
J.U. GRABOW, G.T. FRASER, W.J. LAFFERTY, R.D. SUENRAM, F.J. LOVAS, K.K.
IRIKURA, A.M. ANDREWS, AND J.L. DOMENECH

B 36 The Partially correlated strong collisions model for velocity-and state- changing
collisions. Application to Ar-Broadened HF rovibrational line shape
P. JOUBERT AND D. ROBERT

B 37 Self-Broadening and Shift of Ammonia Transitions Versus Temperature : Theory and Experiments
G. BALDACCHINI, A. CIUCCI, F. D'AMATO, M. DE ROSA, F. PELAGALLI, G. BUFFA, AND O. TARRINI

B 38 Quantum number dependance of the self-broadening coefficients in the ν_1 and ν_3 bands of SO_2
B. SUMPF, O. FLEISCHMANN, M. SCHÖNE, A. KISSEL, AND H.D. KRONFELDT

B 39 The water vapor lineshift investigations at 5μ region
A. VALENTIN, F. RACHET, A. BYKOV, N. LAVRENT'EVA, V. SAVEL'EV, AND L. SINITSA

B 40 Fully Complex Implementation of the Robert-Bonamy Formalism : Halfwidths and Line Shifts of H_2O Broadened by N_2 and O_2
R. LYNCH, R.R. GAMACHE, AND S.P. NESHYBA

B 41 On the Spectroscopic Evidences of $(HF)_n$ Isomeric Structures Formation
E.G. TARAKANOVA AND F. HUISKEN

B 42 Laboratory UV Spectroscopy Applied to Recent UV Observations of the Planets by Spacecraft
J. AJELLO, D. SHEMANSKY, I. KANIK, G. JAMES, X. LIU, S. AHMED, AND M. CIOCCA

B 43 Fine Structure of Infrared Transitions in Solid Hydrogen
R.A. STEINHOFF, M. MENGEL, B.P. WINNEWISSER, AND M. WINNEWISSER

MONDAY, SEPTEMBER 11   14:00

INVITED LECTURES
C

C 1 High Resolution Laser Spectroscopy in the extreme Ultra-Violet (50-100 nm)
W. UBACHS

C 2 Recent Progress in Internal Rotation : What happens above the barrier ?
I. KLEINER

MONDAY, SEPTEMBER 11   16:00 – 18:00

POSTER SESSION
D

D 1 An investigation of the SO molecule by 1+1 REMPI-TOF spectroscopy
     C. BRAATZ AND E. TIEMANN

D 2 High Resolution Laser Spectroscopy of TiO
     C. AMIOT, P. LUC, AND R. VETTER

D 3 FTIR Spectrum of Fundamental band of AsO Radical
     F. ITO, T. NAKANAGA, AND H. TAKEO

D 4 laser Induced Fluorescence of the Blue-Violet Transitions of NiF
     C. DUFOUR AND B. PINCHEMEL

D 5 On the $A^1\Sigma_u^+$ State of Li_2
     F. MARTIN, I. RUSSIER, A.J. ROSS, C. LINTON, P. CROZET, S. CHURASSY, R. BACIS,
     S. MAGNIER, AND M. FRÉCON

D 6 Low-Lying Electronic States of ScCl
     F. TAHER, J. VERGÈS, C. EFFANTIN, A. BERNARD, J. D'INCAN, AND E.A. SHENYAVSKAYA

D 7 Electronic Absorption Spectra of Carbon Chains in Neon Matrices. C_{2n}^-, C_{2n},
     $C_{2n}H$, $HC_{2n+1}H$, and C_{2n+1}
     J. FULARA, D. FORNEY, P. FREIVOGEL, AND J.P. MAIER

D 8 High Resolution Spectroscopy of the Wulf Bands of Ozone
     A.J. BOUVIER, B. BUSSERY, R. BACIS, S. CHURASSY, D. INARD, M. NOTA, J. BRION,
     J. CHARBONNIER, AND J. MALICET

D 9 The ν_2 Band of HOCl
     D. HURTMANS, J. VANDER AUWERA, J.M. FLAUD, AND W.J. LAFFERTY

D 10 The Rotational Spectrum in the Vibrational Ground State of H_2Te
     I.N. KOZIN, S. KLEE, O. POLANZ, AND P. JENSEN

D 11 Temperature Dependance, in the 200-300 K Range, of Vibrational Energy Trans-
     fers in Ozone Excited in the {(200),(101),(002)} Triad
     F. MENARD-BOURCIN, L. DOYENNETTE, J. MENARD, C. BOURSIER, AND C. BOULET

D 12 Fourier Transform Emission Spectroscopy of C_3 : The Renner Effect in the $\tilde{a}^3\Pi_u$
     and $\tilde{b}^3\Pi_g$ Electronics States
     S. CIVIS, D.W. TOKARYK, AND G. HERZBERG

D 13 Simple Modelling of Q-Branch Absorption. Theoretical Model and Application to CO_2 and N_2O
R. RODRIGUES, J.M. HARTMANN, C. BOULET, M. MARGOTTIN-MACLOU, F. RACHET, B. KHALIL, F. THIBAULT, AND J. BOISSOLES

D 14 H_2 ^{18}O Absorption Spectra between 9600 And 16000 cm^{-1}
J.M. FLAUD, C. CAMY-PEYRET, J.Y. MANDIN, A. BYKOV, O. NAUMENKO, T. PETROVA, L. SINITSA, AND A. SCHERBAKOV

D 15 High Resolution Study of the IR Spectrum of the PF_3 Molecule between 645 and 730 cm^{-1}
M. BADAOUI, N. BEN SARI-ZIZI, H. NAJIB, AND G. GRANER

D 16 The Microwave Spectrum of IN_3
H.O. MUNZ, H.K. BODENSEH, AND T.M. KLAPÖTKE

D 17 Assignment of Methyl Cyanide Far Infrared Laser Lines
H. SARKKINEN, J. PIETILÄ, R.PASO AND R. ANTTILA

D 18 High Resolution FTIR and Photoacoustic Spectra of Monoiodoacetylene
M. SAARINEN, A. JUTILA, P. JUNGNER, O. VAITTINEN, AND L. HALONEN

D 19 Line Intensities in the Far Infrared Spectrum of H_2O_2
A. PERRIN, J.M. FLAUD, C. CAMY-PEYRET, R. SCHERMAUL, M. WINNEWISSER, J.Y. MANDIN, V. DANA, M. BADAOUI, AND J. KOPUT

D 20 Semi-classical Line-widths Calculations for Rovibrational Lines of $^{12}CH_4$ Perturbed by a Rare Gas
T. GABARD

D 21 A Tensorial Formalism Adapted to Octahedral molecules or Ions Having an Odd Number of Electrons
V. BOUDON AND F. MICHELOT

D 22 Determination of Induced Dipole Moments in the $v_3 = 2$ State of Methane by Linear Stark Effect
M. LOËTE, M.P. COQUARD, H. SASADA, AND Y. KUBA

D 23 A New Semirigid Bender Model for the HCNO Molecule
T. FLÖCK AND P. JENSEN

D 24 Extended Measurements of the Millimeter Wave Spectrum of H_2COH^+ and its Isotopomers
L. DORE, G. CAZZOLI, S. CIVIS, AND F. SCAPPINI

D 25 High resolution Spectrum of Fluochloreothyne between 200 and 700 cm^{-1}
H. BÜRGER AND M. SENZLOBER

D 26 FTIR-Investigation of ^{15}N-Triazine : Ground State Constants and Rovibrational Analysis of the $\nu_{10}/2\nu_{14}$ Band System
W. BODENMÜLLER, H. ESSIG, A. RUOFF, J. BEHREND, M. KOIVUSAARI, S. ALANKO, R. SCHRODERUS, R. ANTTILA, J. WALRAND, AND G. BLANQUET

PROGRAM OF SESSIONS

D 27 High Resolution Infrared Fourier Transform Spectroscopy of Pyrrole (C_4H_5N)
A. HELD, A. MELLOUKI, AND M. HERMAN

D 28 The Anomeric Effect in Trifluoromethoxy methane, CF_3OCH_3
R. KÜHN, D. CHRISTEN, H.G. MACK, D. KONIKOWSKI, R. MINKWITZ, AND H. OBER-HAMMER

D 29 Torsional Excited States in the Microwave Spectrum of Trans-2,3-Dimethyloxirane

H. HARTWIG AND H. DREIZLER

D 30 The Curl-Dane-Watson Procedure with Damping for Calculating the Molecular Parameters
M. RYTEL AND T. RYTEL

D 31 Self Pressure Broadening in Ammonia : Cars and IRp Spectra of the ν_1 Bands of $^{14}NH_3$, $^{15}NH_3$, $^{14}ND_3$, and $^{15}ND_3$
S.W. ANDERS, J. JONUSCHEIT, D. ILLIG, K. SARKA, M. STAMOVA, H.W. SCHRÖTTER, D. BERMEJO, AND J. SANTOS

D 32 Effect of Dicke Narrowing and Velocity Averaging of Collisional Cross Sections on CO Pressure Broadened Line Profile
A. HENRY, M. MARGOTTIN-MACLOU, D. HURTMANS, J.P. BOUANICH, AND A. VALENTIN

D 33 Theoretical Calculations of Pressure Broadening Coefficients for H_2O Perturbed by Hydrogen or Helium Gas
R. GAMACHE AND J.B. POLLACK

D 34 Line Coupling in Anisotropic Raman Q Branches : Application to the $\nu_1/2\nu_2$ Fermi Dyad of CO_2
L. BONAMY, B. LAVOREL, G. FANJOUX, AND G. MILLOT

D 35 The Electric Dipole moment of Ammonia Dimer for $G :| K |= 1$ (band origin 747.2 GHz)
G. COTTI, H. LINNARTZ, AND W.L. MEERTS

D 36 Semiempirical Model of the Cooperativity Effect in the Conjugated Hyrogen-bond Bridges A-H...B
G.V. YUKHNEVICH

D 37 Multi-Nozzle jet Fourier Transform Spectroscopy
R. GEORGES, M. BACH, AND M. HERMAN

D 38 Retrieval of Vertical Concentration Profiles of Stratospheric Constituents from Balloon-Borne Fourier Transform Spectroscopy
S. PAYAN, C. CAMY-PEYRET, P. JESECK, T. HAWAT, AND G. DURRY

D 39 Novel Methods for Quantitative Gas Analysis at Millimetric Wavelengths
N.D. REZGUI, J.G. BAKER, J. ALLEN, AND J.F. ALDER

D 40 Information System Airsentry for Modeling Radiative Transfer in the Atmosphere, Based on High Resolution Molecular Spectra
V.F. GOLOVKO, A.V. NIKITIN, A.A. CHURSIN, AND V.G. TYUTEREV

D 41 Temperature Dependent UV-VIS Cross Sections of NO_2 and O_3 for the Global Ozone Monitoring Experiment Onboard the Environmental Research Satellite -2
A. DEHN, B. DETERS, S. HIMMELMANN, A. TUERK, M. WEISSENMAYER, AND J.P. BURROWS

D 42 Rotation-Torsion Effective Hamiltonian for Dinitrogen Pentoxide
M. KREGLEWSKI

D 43 Retrieval of Spectral Line Parameters in PA-Spectr oscopy of Derivative with the two-Frequency Laser
V.A. KAPITANOV, M.Y. KATAEV, AND O.Y. NIKIFOROVA

TUESDAY, SEPTEMBER 12   9:00

INVITED LECTURES

E

E 1 Rotational Spectroscopy of B...XY in pre-reactive mixtures of Lewis Bases B and Halogens or Interhalogens XY
A.C. LEGON

E 2 Single Molecule Spectroscopy in Low-Temperature Solids : A Review
B. LOUNIS, P. TAMARAT, R. BROWN, AND M. ORRIT

TUESDAY, SEPTEMBER 12   10:30 – 12:30

POSTER SESSION

F

F 1 An Ab Inition Calculation of the Rovibronic Energies of the CH_2^+ Molecule
P. JENSEN, M. BRUMM, W.P. KRAEMER, AND P.R. BUNKER

F 2 Observation of high J Values in the $v' = 2,3,4$ and 5 Vibrational Levels of the Photodissociation Spectrum of the b←a System of O_2^+
M. LARZILLIÈRE, C. FRIGON, C.J. DELISLE, N. VARFALVY, AND P.C. COSBY

F 3 The $D^2\Sigma^+ - X^2\Sigma^+$ Transition of The CaBr and CaI Radicals
E. CASERO-JUNQUERA, D. BENHABIB, J. ROSTAS, AND G. TAIEB

F 4 High Resolution Spectroscopic Analysis of $EO_g^+ \to A1_u(^3\Pi_u)$ and $EO_g^+ \to B"1_u(^1\Pi_u)$
Transitions in the I_2 molecule
R. BACIS, S. CHURASSY, D. INARD, M. NOTA, AND V. SKOROKHODOV

F 5 Spectroscopy of CrCl : Observation and Analysis of Three Band Systems in the
Near Infrared
R. KOIVISTO AND O. LAUNILA

F 6 The ν_2, ν_6, and ν_7 Fundamentals of NC-CC-CN
F. WINTHER

F 7 Laserspectroscopy of the B — X Transition of KAr
H. VALIPOUR AND D. ZIMMERMANN

F 8 Spin-Orbit Interactions Between $c^3\Sigma^+$ and $B^1\Pi$ States of ScF and ScCl : Effects
on the Fine and hyperfine Structures
M.A. LEBEAULT-DORGET, F. TAHER, C. EFFANTIN, A. BERNARD, J. D'INCAN,
E.A. SHENYAVSKAYA, AND J. VERGÈS

F 9 High Resolution Electron Impact Study of the Emission Spectrum of Molecular
Hydrogen
X. LIU, S.M. AHMED, G.K. JAMES, J.M. AJELLO, D.E. SHEMANSKY, H.Y. HU,
H. ABGRALL, E. ROUEFF, F. LAUNAY, AND J.Y. RONCIN

F 10 Effective Operators Approach for Global Treatment of Vibrational-Rotational
Spectra of Nitrous Oxide
V.I. PEREVALOV, O.M. LYULIN, AND J.L. TEFFO

F 11 Laser optogalvanic Study of HCO $(\tilde{A}^2A" - \tilde{X}^2A')$ Using a Ti:Sapphire Laser
J.L. DESTOMBES, I. HADJ BACHIR, T. HUET, AND A. ZELLAGUI

F 12 Bifurcation in Rotanial Spectra of Nonlinear AB_2 Molecules
I.N. KOZIN AND I.M. PAVLICHENKOV

F 13 Millimeter-Wave and Infrared Spectroscopy of $BrC^{15}N$: Equilibrium Structure of
Cyanogen Bromide
F. TAMASSIA, C. DEGLI ESPOSTI, L. DORE, AND G. CAZZOLI

F 14 H_2S Spectrum from 0.9 to 5 μm : the Polyade Structure and Spectroscopic Pa-
rameters
L.R. BROWN, J. CRISP, D. CRISP, A. BYKOV, O. NAUMENKO, M. SMIRNOV, L. SINITSA,
AND A. PERRIN

F 15 NIR Spectral Bands of Acetylene Measured by high Resolution Diode Laser Spec-
troscopy : $\nu_1 + 3\nu_3$ and $\nu_1 + 2\nu_2 + \nu_3 + 4\nu_4^0$ revisited
J.G. BAKER, D. LI, AND N.J. BOWRING

F 16 Assignment and Preliminary Analysis of the IR Absorption Spectrum of CH_3D
in the Region 1900-3200 cm^{-1}
A. NIKITIN, J.P. CHAMPION, V.G. TYUTEREV, AND L.R. BROWN

F 17 A Detailed Analysis of the $\nu_2/\nu_5/\nu_3 + \nu_6$ Band System of $^{13}CH_3I$ and $^{12}CH_3I$
S. ALANKO

F 18 Fourier Transform Microwave Spectroscopy of Stibine in the Ground, $v_2 = 1$, and
$v_4 = 1$ Vibrational States. Extension of the Effective Hyperfine Hamiltonian
H. HARDER, C. GERKE, L. FUSINA, AND G. DI LONARDO

F 19 Tunable far Infrared Spectroscopy of H_2O_2
G. DI LONARDO, L. FUSINA, E. VENUTI, M. BELLINI, E. CATACCHINI,
P. DE NATALE, AND M. INGUSCIO

F 20 Analysis of the Rotation-Vibration in the $v_2 = 1$, $v_3 = 1$, $v_5 = 1$ and $v_6 = 1$ states
of the CDF_3
J. COSLEOU, J. DEMAISON, M. KHELKHAL, H. FICHOU, M. PAPLEWSKI, H. BÜRGER,
C. GERKE, AND H. HARDER

F 21 Seminumerical Contact Transformation : Form Internal Coordinate Rovibrational
Hamiltonian to Effective Rotational Hamiltonians. Framework of The Method
T.J. LUKKA AND E. KAUPPI

F 22 New Treatment of a two Oscillator System. Application to molecular Doubly
Degenerate Vibrational Modes
V. BOUJUT AND F. MICHELOT

F 23 Some New Aspects in the local mode and Near Local Mode Approaches in Molecules

O.N. ULENIKOV AND R.N. TOLCHENOV

F 24 Microwave Spectra and Structure of $CF_2=NH$ and $CF_2=NCl$
P. GRONER, J.R. DURIG, AND D.D. DESMARTEAU

F 25 Rotational and Rovibrational Spectra of $CHClF_2$ in all States with Population
Factors > 4 % and of its ^{13}C Isotopomer
S. BLANCO, G. CAZZOLI, J.M. COLMONT, G. COTTI, G. GRANER, Z. KISIEL, I. MERKE,
AND L. PSZCZOLKOWLKI

F 26 Analysis of the ν_3 Band of ND_2H
L. FRANCOU, F. RACHET, A. VALENTIN, AND L.H. COUDERT

F 27 High Resolution FTIR Spectrum of Thiocarbonyldifluorid SCF_2
H. BÜRGER AND W. JERZEMBECK

F 28 Microwave Spectrum of SY N Oxalyl Fluoride
K.M. MARSTOKK AND H. MOLLENDAL

F 29 Five-Membered Cyclic Ketones : The Rotational Spectra of Isotopic Substituted
Cyclopentenones
R. RUOFF, A. KREBS, T. SCHAEFFLER, G. STIEGLER, AND H.K. BODENSEH

F 30 Free Jet Absorption Millimeterwave Spectrum of Thioanisole
B. VELINO, S. MELANDRI, W. CAMINATI, AND P.G. FAVERO

F 31 The Microwave Spectrum of ABCO-H$_2$O and DABCO-H$_2$O Determined by Molecular Beam Fourier Transform Microwave Spectroscopy
D. CONSALVO AND W. STAHL

F 32 Application of Evolution Strategies in Nonlinear Least-squares fit procedures for Spectroscopic data
Y. HEINER, J. WASCHULL, B. SUMPF, AND H.D. KRONFELDT

F 33 Line Broadening and Shift in the ν_3 $^{12}CO_2$ and $^{13}CO_2$ Bands
S. MARCHETTI AND R. SIMILI

F 34 Pressure Broadening in the ν_{14} band of benzene
J. WASCHULL, Y. HEINER, B. SUMPF, AND H.D. KRONFELDT

F 35 Analysis of the Branch Shapes in CO_2 15μm Spectrum
N.N. FILIPPOV AND M.V. TONKOV

F 36 N$_2$-Broadening Coefficients in the ν_3 Band of CH$_3$D
J. WALRAND, G. BLANQUET, AND J.P. BOUANICH

F 37 M_J Dependence of Collisional Transition between Fine-Structure Levels of $K(4P^2P_{j,M_J})$ Atom
J. KAWAI, K. MATSUBARA, T. KOKITA, H. KATO, AND M. BABA

F 38 Spectral Hole Burning, Resonant Two Photon Ionization and High Resolution Dispersed Fluorescence as a Probe of Intermolecular Vibrations in Hydrogen Bonded Molecular Complexes
K. KLEINERMANNS, M. SCHMITT, U. HENRICHS, CH. DEUSEN, CH. JACOBY, M. GERHARDS, AND W. PERL

F 39 Observation of Strong Coriolis Coupling in the IR-Spectrum of Ar-CO
S. KÖNIG, G. HILPERT, AND M. HAVENITH

F 40 (Several?) Electronic States of NiCl$_2$ in the 360nm region measured at rotational resolution
G. VAN DEN HOEK AND J.M. BROWN

F 41 Spectroscopy with the Cologne Terahertz Spectrometer up to Frequences of 1.27 THz
S.P. BELOV, T. KLAUS, H. KLEIN, E. KLISCH, R. SCHIEDER, G. WINNEWISSER, AND E. HERBST

F 42 Getting the Information you need
J. VOGT, W. HUTTER, AND N. VOGT

F 43 Direct Absorption Measurements of Ar–CO Rotational transitions with a Supersonic Jet mm–Wave Spectrometer
M. HEPP, W. JÄGER, I. PACK AND G. WINNEWISSER

TUESDAY, SEPTEMBER 12   14:00

INVITED LECTURES
G

G 1 Networks of Anharmonic Resonances in the High Resolution Spectrum of HCNO
M. WINNEWISSER AND S. ALBERT

G 2 Double-Resonance Vibrational Overtone Spectroscopy of Jet-Cooled Molecules Using IRLAPS Detection
O.V. BOYARKIN, L. LUBICH, D.S. PERRY, AND T.R. RIZZO

TUESDAY, SEPTEMBER 12   16:00 – 18:00

POSTER SESSION
H

H 1 Generalized Quantum Defect Theory at Low Energies
F. TEXIER AND C. JUNGEN

H 2 Fast Ion Beam High Resolution Laser Induced Fluorescence Spectrum of $B^4\Sigma_u^-$ - $X^4\Sigma_g^-$ Transition of the C_2^{+1}
K. BOUDJARANE, M. LARZILLIÈRE, AND M. CARRÉ

H 3 The Ultra-Violet and Infrared Spectrum of the NCN Radical
K.D. HENSEL, S.A. BEATON, Y. ITO, AND J.M. BROWN

H 4 Hyperfine Constants of BrF and IF
H.S.P. MÜLLER AND M. GERRY

H 5 Spectroscopy of CrF : recent Results on the $A^6\Sigma^+ - X^6\Sigma^+$ and $B^6\Pi - X^6\Sigma^+$ Band Systems in the Near Infrared
S. WALLIN, R. KOIVISTO, AND O. LAUNILA

H 6 The ν_1 Band System of HCCCN
F. WINTHER, S. NAIM, L. MBOSEI, AND A. FAYT

H 7 The $B^2\Sigma$ Interaction Potential of LiAr Deduced from Laserspectroscopic Data
R. BRUEHL AND D. ZIMMERMANN

H 8 A Re-investigation of the $A^2A_1 - X^2B_1$ Transitions of NH_2 and H_2O^+ in the Near Infrared Region
T. HUET, I. HADJ BACHIR, J.L. DESTOMBES, AND M. VERVLOET

H 9 Proton Rearrangement Dynamics and Spectrum of CH_3^+
P.R. BUNKER

H 10 Effective operators Approach for Global Treatment of Vibrational-Rotational Spectra of Carbon Dioxide
J.L. TEFFO, V.I. PEREVALOV, O.M. LYULIN, E.I. LOBODENKO, AND O.N. SULAKSHINA

H 11 High Precision Measurement of the Dipole Moment of HOCl by Tunable FIR Stark Spectroscopy
G. MODUGNO, P. DE NATALE, M. BELLINI, M. INGUSCIO, G. DI LONARDI, L. FUSINA, M. GODEFROID, AND J. VANDER AUWERA

H 12 Line Strenghts for HeH_2^+
M. JUREK, V. SPIRKO, AND W.P. KRAEMER

H 13 Intensities Measurements of Ozone Lines in the ν_3 Band by Tunable Diode Laser Spectrometry
M.R. DE BACKER AND D. COURTOIS

H 14 The Onset of Vibronic Chaos in NO_2 between 10000 cm^{-1} and 17000 cm^{-1}
M. BATHELEMY, A. DELON, R. JOST, AND J. LIEVIN

H 15 Rovibronic Interactions in NO_2
J. NYGARD, A. DELON, AND R. JOST

H 16 Evolutions of Rovibronic Levels of Jet cooled NO_2 in High Magnetic Field
A. PASINSKI, F. BYLICKI, A. DELON, AND R. JOST

H 17 Irreducible Vibrational Operators Adapted to Complex Band Systems of Polyatomic Molecules. Associated Algorithms and Programs. Application to the T_D, O_H, and C_3V Groups
A. NIKITIN, J.P. CHAMPION, AND VL.G. TYUTEREV

H 18 Precise Study of $2\nu_5$ Hybrid Band of CHD_3
O.N. ULENIKOV

H 19 High Resolution Study of the IR Spectrum of PF_3 Molecule between 1150 and 1400 cm^{-1}
R. SEBIHI, H. NAJIB, AND N. BEN SARI-ZIZI

H 20 "Ritz" Analysis of the FT-IR Spectrum of $^{13}CH_3OH$ from 25 to 350 cm^{-1}
G. MORUZZI AND J.C.S. MORAES

H 21 Spectroscopy of the Ground and Excited Electronic States of IrF_6
V. BOUDON AND M. ROTGER

H 22 Algebraic Treatment of Bending Modes of Tetrahedral Molecules through the Chain $U(6) \supset U(5) \supset U(3) \times U(2) \supset SO(3) \times SO(2) \supset SO(2)' \times SO(2)"$
V. BOUJUT AND F. MICHELOT

H 23 Intramolecular Potential Function of Methane Molecule as the Result of Global Fit its High- Resolution Vibration-Rotation Spectra
O.N. ULENIKOV AND R.N. TOLCHENOV

H 24 Torsion-Rotational Hamiltonian of an Nonrigid Molecule with two Nonequivalent
Tops with a Common Axis of Rotation
A.V. BURENIN

H 25 Internal Rotation and Low-Energy Skeletal Vibrations in Acetone
Z. DUTKIEWICZ AND J. KOPUT

H 26 Stabilization of Intermediate Inertial Axis of Asymmetric Top Molecule by Orbit-
ing Rydberg Electron
I.M. PAVLICHENKOV

H 27 $^{12}CD_3F$ and $^{13}CD_3F$: Combined Analysis of the Rotational and Infrared Spectra
of four Interacting Bands $2\nu_2(A_1)$, $\nu_3(A_1)$, $\nu_5(E)$, and $\nu_6(E)$
I. MERKE, J. DEMAISON, J. LUMMILA, AND L. HALONEN

H 28 Classical and Quantum Phase Spaces for a Molecule with Internal Rotation
J. ORTIGOSO AND J.T. HOUGEN

H 29 Anharmonicity Constants of Benzene : CARS Spectra of CH- and CD-Stretch
Bands of C_6H_6, C_6D_6, $s - C_6H_3D_3$, $o-$, $m-$, $p - C_6H_4D_2$, C_6HD_5
T. MANGOLD AND H.W. SCHRÖTTER

H 30 The Rotational Spectrum of Ethylarsine
P. DREAN, J.C. LOPEZ, J.L. ALONSO, AND J. DEMAISON

H 31 ^{33}S- Nuclear Quadrupole Coupling Constants determined by Molecular Beam
Fourier Transform Microwave Spectroscopy - A Comparative Study -
U. KRETSCHMER, H. HARTWIG, N. HANSEN, AND H. DREIZLER

H 32 Characterization of the Monohalogenophosphanes by High Resolution Infrared
and Millimeterwave Spectroscopies
M. PAPLEWSKI, P. DREAN, J. DEMAISON, H. BÜRGER, AND H. BECKERS

H 33 Modeling of the Temperature Dependence in the ν_5 $^RQ_0$-Branch Absorption of
CH_3Cl
F. FRICHOT, J.M. HARTMANN, AND N. LACOME

H 34 The Calculation of Spectral Lineshapes in presence of Collisional Coupling
S. BELLI, G. BUFFA, AND O. TARRINI

H 35 Model Band Shape with Varied Branch Coupling for Atmospheric Applications
M.V. TONKOV, N.N. FILIPPOV, YU.M. TIMOFEYEV, AND A.V. POLYAKOV

H 36 Ar-Broadening Coefficients in the ν_2 Band of HCN
J.P. BOUANICH, G. BLANQUET, AND J. WALRAND

H 37 Observation of a Non-Thermal Ortho-Para Ratio of H_3^+ in Hydrogen Plasmas
D. UY, M. CORDONNIER, R.M. DICKSON, K.E. KERR, AND T. OKA

H 38 The Microwave Spectrum of the Open-Shell Complex NO-HF
C.R. DENNIS, C.J. WHITHAM, AND B.J. HOWARD

H 39 The $CO:CO_2$ Complex in Solid Argon
V. RADUCU, D. JASMIN, P. BROSSET, R. DAHOO, B. GAUTHIER-ROY, AND L. ABOUAF-MARGUIN

H 40 A High Resolution and High Contrast Spectrometer to Competer with (Fourier Transform) Interferometers
P. EVRARD AND J.L. STEHLE

H 41 High Resolution Wavenumber Standards for the Infrared. (UPAC Recommendations 1995)
G. GUELACHVILI ET AL.

H 42 Development of a Hollow Cathode/Ring-Down Spectrometer : Characterization of Carbon Containing Species
M. KOTTERER, J. SLOTTERBACK, AND J.P. MAIER

H 43 Near Infrared Spectroscopy at 1.5 μm Using a Herriott Multipass Cell
L.F. HOWIESON, G. DUXBURY, N. MARTIN, T. GARDINER, AND P.T. WOODS

WEDNESDAY, SEPTEMBER 13   9:00

INVITED LECTURES

J

J 1 Optical Stark and PPMODR Studies of Metal Containing Molecules
T.C. STEIMLE, A.J. MARR, M. FLORES AND B. LI

J 2 Molecular Spectroscopy and the Accurate Measurement of Intensities using Fourier Transform Instruments
J. VANDER AUWERA

WEDNESDAY, SEPTEMBER 13   10:30 – 12:30

POSTER SESSION
K

K 1 Ab initio Interpretation of the I.R. Spectrum of N_2O_4 in the region 300-600 cm^{-1}
Y. EL YOUSSOUFI, J. LIEVIN, B.P. WINNEWISSER, J.W.G. SEIBERT, AND M. HERMAN

K 2 Fourier Transform Spectroscopy and Photoassociation Spectroscopy of Cold
Atoms : the $Rb_2^1\Pi_g$ and 0_g^1 Electronic States Potential Energy Curves up to
100 $\mathring{A}$
C. AMIOT

K 3 Dunham Series Coefficients up to 20-TH Order
M. RYTEL AND T. RYTEL

K 4 Spin-Orbit Splittings in Calcium Monohalides. A Relativistic Ligand Field Approach
M. BENCHEIKH

K 5 REMPI Spectroscopy of the $E^1\Pi$ and $C^1\Sigma^+$, $v = 0$ and $v = 1$ States of $^{12}C^{16}O$
and $^{13}C^{16}O$ Accidental Predissociation Phenomena
P. CACCIANI, W. HOGERVORST, AND W. UBACHS

K 6 Theoretical Study of the Electronic Structure of BaK
N. BOUTASSETTA, A.R. ALLOUCHE, AND M. AUBERT-FRÉCON

K 7 Investigation of the $e^6\Pi$ - $a^6\Delta$ Transition in the Green System of FeH at 532 nm
D.M. GOODRIDGE, R.T. CARTER, AND J.M. BROWN

K 8 Fast Ion Beam Laser Spectroscopy of $^{13}CO_2^+$: Laser Induced Fluorescence of the
$\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$ Electronic transition
M. LARZILLIÈRE, A. RONEY, AND N. VARFALVY

K 9 $S_1 - S_0$ Spectroscopy and S_1 Dynamics of 4- and 5-Methylpyrimidine
H. BITTO AND S. GFELLER

K 10 New Refined Potential Energy Surfaces for H_2O and H_2S
O.L POLYANSKY, P. JENSEN, AND J. TENNYSON

K 11 High Resolution Fourier Transform and Diode Laser Spectra of the 1940 cm^{-1}
Band System of COF_2 at Stratospheric Temperatures
G. DUXBURY, M. MCPHAIL, AND R. MCPHEAT

K 12 Accounting for the Anomalous Centrifugal Distortion in the HDO Molecule
L.H. COUDERT

K 13 High-Order Derivatives of the Dipole Moment Function for the Ozone Molecule
O. SULAKSHINA, VL.G. TYUTEREV, AND A. BARBE

K 14 H_2Te : High Resolution Study of the ν_1, ν_3 and $\nu_1 + \nu_2$, $\nu_2 + \nu_3$ Bands
J.M. FLAUD, PH. ARCAS, M. BETRENCOURT, H. BÜRGER, AND O. POLANZ

K 16 Observation and Calibrations of NIR lines of Water using a Diode Laser Spectrometer
T.D. BEVIS, J.G. BAKER, AND N.J. BOWRING

K 16 Studies on the Infrared Spectrum of H_2S
O.N. ULENIKOV, A.B. MALIKOVA, G.A. ONOPENKO, S. ALANKO, M. KOIVUSAARI, AND R. ANTTILA

K 17 Effective Hamiltonian for Inversion-Rotation States of Ammonia-Like Molecules
K. SARKA AND H.W. SCHRÖTTER

K 18 High Resolution Infrared Study of the MID-IR and CH-Stretching Regions of $H_2C={}^{13}C=CH_2$
F. HEGELUND, O. POLANZ, AND H. BÜRGER

K 19 High-resolution FTIR Study of the $\nu_2 + \nu_4$ and $\nu_4 + \nu_5$ Rovibrational bands of CH_3 ${}^{79}Br$ between 4200 and 4600 cm^{-1}
N. BEN SARI-ZIZI AND C. ALAMICHEL

K 20 Diode-Laser Spectroscopy : Absolute line Intensities of ν_3 Band of ${}^{12}CH_3F$ at 9.6 μm
M. LEPERE, G. BLANQUET, AND J. WALRAND

K 21 Force Field and Dipole Moment Derivatives of Methane
A. MOURBAT AND M. LOËTE

K 22 Determination of Induced Dipole Moments in the ν_2/ν_4 Dyad of SnH_4 by Linear Stark Effect
M. LOËTE, M.P. COQUARD, Y. OHSHIMA, AND M. TAKAMI

K 23 Hot Bands in the Region of the Bending Vibrations ν_4 and ν_5 of HHCl
A.M. TOLONEN

K 24 Vibrational Analysis of the Infrared Spectra of $ClONO_2$ and $BrONO_2$: Harmonic Force of the Halogen Fields of the Halonen Nitrates
J. ORPHAL, M. MORILLON-CHAPEY, AND G. GUELACHVILI

K 25 The High-Precision Laboratory Frequency Measurements of the Interstellar Molecules Rotational Spectra in the 70 ÷ 155 GHz Frequency Range
E.A. ALEKSEEV, O.I. BASKAKOV, S.F. DYUBLKO, M.N. EFIMENKO, V.A. EFREMOV, V.V. ILYUSHIN, AND S.V. PODNOS

K 26 High-Resolution Fourier-Transform Infrared Spectroscopy of the ν_4 and $2\nu_4$ Bands of $CH_2=CHF$
A. DE LORENZI, S. GIORGIANNI, AND P. STOPPA

K 27 Fermi Resonance and Coriolis Coupling Between ν_5 and $2\nu_6$ in CH_2 ${}^{35}ClF$
S. BLANCO, J.C. LESARRI, J.C. LOPEZ, J.L. ALONSO, AND A. GUARNIERI

K 28 Gas Phase Infrared Spectra of Aromatic Molecules. Force Field Ab Initio Calculation and Complete Spectrum Assignment
E. CANÉ, P. PALMIERI, A. TARRONI, AND A. TROMBETTI

K 29 Equatorial-Axial Conformational Equilibrium in 1-Fluoro-1-Silacyclobutane and Fluorocyclobutane
S. MELANDRI AND L.B. FAVERO

K 30 Investigation of the Speed Dependence of Rotational Relaxation Using a Microwave Spectrometer with a Circular Waveguide : Studies on Nitrous Oxide
T. KÖHLER, H. MÄDER, AND A SCHWENK

K 31 Centimeter and millimeter-Wave Spectrum of Selected Isotopomers of Acrylonitrile. ^{14}N Quadrupole and Spin-Rotation Constants. Structure Determination
J.M. COLMONT, G. WLODARCZAK, I. MERKE, H.S.P. MÜLLER, E.H. TIEN, R.J. RICHARDS, AND M.C.L. GERRY

K 32 Pressure Broadening of the ν_3 Band of CO_2 at crygenic Temperatures
D. NEWNHAM, J. BALLARD, AND M. PAGE

K 33 The First Observation of Field Free $\Delta l = 2$, $f - e$ Transitions in HCN
A. MAKI, W. QUAPP, S. KLEE, AND G. MELLAU

K 34 Line Shift and Line Asymmetry Interdependence for the H_2O Specrtral Lines
L.I. NESMELOVA, Y.N. PONOMAREV, O.B. RODIMOVA, AND S.D. TVOROGOV

K 35 H_2O Broadened by CO_2 for Application to Planetary Atmospheres
R.R. GAMACHE, S.P. NESHYBA, J.J. PLATEAUX, A. BARBE, L. REGALIA, AND J.B. POLLACK

K 36 A High Precision Technique for Pressure Line Shifts Measurements : Application to NH_3 and HCN
F. RAYNAUD, A. BABAY, V. LEMAIRE, AND B. LEMOINE

K 37 High Resolution UV Spectroscopy of Phenol and the Hydrogen Bonded Phenol/Water Cluster
G. BERDEN, L. MEERTS, M. SCHMITT, AND K. KLEINERMANNS

K 38 Diode Laser Spectra of Ar-CH_4 Complexes in the 7 μm Region Observed with a New Double Modulation Technique
I. PAK, M. HEPP, D. ROTH, AND G. WINNEWISSER

K 39 High Resolution Spectroscopy of Methyl Iodide Using a Novel Doppler-Free Technique
S. CAROCCI, A. DI LIETO, A. MENCIASSI, P. MINGUZZI, F. QUOCHI, AND M. TONELLI

K 40 Interactivity Laser Spectroscopy of Excited Atoms and Molecules
V. SERDYUKOV, L. SINITSA, Y. POPLAVSKII, AND A. TOBOLKIN

K 41 Saturation Spectroscopy near 3000 cm^{-1} using Frequency-Offset-Locked CO-Overtone Laser Sideband Spectrometer
M. MÜRTZ, B. FRECH, P. PALM, M.H. WAPPELHORST, W. URBAN, J. LEGRAND,

AND F. HERLEMONT

K 42 Application of Orotron Intracavity Millimiter- Wave Spectrometer for Gas Analysis
B.S. DUMESH, V.D. GORBATENKOV, AND L.A. SURIN

K 43 Precise Lines Shape Measurements by Tunable Diode Laser
A.I. NADEZHDINSKII

THURSDAY, SEPTEMBER 14   9:00

INVITED LECTURES

L

L 1 Spectroscopy and Reactions in (Halogenated-Benzene)-$(NH_3)_n$ Clusters
C. JOUVET, S. MARTRENCHARD-BARRA, C. DEDONDER-LARDEUX, D. SOLGADI, P. MILLIE, AND V. BRENNER

L 2 Spectroscopy of the Earth's Stratosphere : Measurements of the HO_X, NO_X, and CL_X Radical Chemistries
K. CHANCE

THURSDAY, SEPTEMBER 14   10:30 – 12:30

POSTER SESSION

M

M 1 An ab initio Study on the Equilibrium Structure and Torsional Potential Energy Function for Hydrogen Peroxide and Dinitrogen Tetroxide
J. KOPUT

M 2 MMW Spectroscopy of Reactive Species Produced by laser Photolysis
M. CORDONNIER, M. BOGEY, A. WALTERS, AND B. DELCROIX

M 3 REMPI Spectroscopy on AlO
A. MARIJNISSEN AND J.J. TER MEULEN

M 4 Analytical Treatment of highly Excited Vibration- Rotational States of Diatomic Molecules
A.V. BURENIN AND M.Y. RYABIKIN

M 5 Seven BaCl Electronic States by L.I.F.F.T.S
M. HAFID, J. VERGÈS, AND C. AMIOT

M 6 Theoretical Study of the Electronic Structure of Sr_2
N. BOUTASSETTA, A.R. ALLOUCHE, AND M. AUBERT-FRÉCON

M 7 New Rydberg-Transitions of the ArH and ArD Molecules
I. DABROWSKI, D. TOKARYK, M. VERVLOET, R.H. LIPSON, AND J.K.G. WATSON

M 8 Fermi Resonance and Singlet Triplet Perturbations in The Spectrum of Singlet Methylene
A. ALIJAH, G. DUXBURY, M. VAN GOGH, AND B. MCDONALD

M 9 Rotational Analysis of two Electronic Transitions of NiCl
C. DUFOUR, B. PINCHEMEL, AND M. VERVLOET

M 10 Global Rovibrational Analysis of Cyanogen Fluoride (FCN)
K. FARKSI, I. DUBOIS, H. BREDOHL, AND A. FAYT

M 11 A Dipole Moment Function for the Water Molecule Determined from Experimental Rovibrational Line Intensities in a Variational Approach
S. TASHKUN, VL.G. TYUTEREV, AND P. JENSEN

M 12 The Emission Spectrum of Hot Water in the Region between 370 and 930 cm^{-1}
O.L. POLYANSKY, J.R. BUSLER, B. GUO, Z. KEQING, AND P.F. BERNATH

M 13 Infrared Spectra of Ozone in the 4300 cm^{-1} Region. Analysis of the $3\nu_1 + \nu_3$ Band including $2\nu_1 + 3\nu_2$ Dark Band
O. SULAKSHINA, A. BARBE, VL.G. TYUTEREV, AND J.J. PLATEAUX

M 14 TF Spectra of Isotopic Carbon Disulfide : the $3\nu_3$ Band of $^{12}C^{34}S_2$ and $^{13}C^{32}S_2$
G. BLANQUET, J. WALRAND, J.F. BLAVIER, H. BREDOHL, AND I. DUBOIS

M 15 A New Rovibrational Analysis of the ν_2 and ν_5 Infrared Bands of H_3Si^79Br
A. CEAUSU, G. GRANER, H. BÜRGER, AND P. PRACNA

M 16 Water Vapor Absorption in a Millimeter Wave Atmospheric Window
A. BAUER, M. GODON, J. CARLIER, AND R. GAMACHE

M 17 Near Infrared Absorption of Ammonia at High Pressure
L. LUNDSBERG-NIELSEN, M. NICOLAISEN, AND J. HENNINGSEN

M 18 The Rovibrational Spectrum of AsF_3. A combined High Resolution Infrared and Millimeterwave Study
H. BÜRGER, J. RADTKE, H. RULAND, P. DREAN, AND J. DEMAISON

M 19 FTIR Study of the second Stretching Vibrational Overtone System of H_3 ^{70}GeD : Example of an almost Asymmetric Rotor Band
H. BÜRGER AND L. HALONEN

M 20 High-resolution FTIR Study of the $\nu_1 + \nu_5$, $\nu_2 + \nu_3 + \nu_4 - \nu_3$ and $\nu_3 + \nu_4 + \nu_5 - \nu_3$ rovibrational bands of $CH_3^{79}Br$
N. BEN SARI-ZIZI AND C. ALAMICHEL

M 21 High Resolution Room Temperature Study of the $2\nu_1 - \nu_1$ Rovibrational Transitions of CH_4 by Stimulated Raman Pumping-Inverse Raman Spectroscopy
D. BERMEJO, R.Z. MARTINEZ, J. SANTOS, J.P. CHAMPION, AND J.C. HILICO

M 22 Ground State Axial Rotational Constants of $^{12,13}CH_3I$ and $^{12,13}CD_3I$
M. KOIVUSAARI, S. ALANKO, J. PIETILA, V.M. HORNEMAN, R. PASO, AND R. ANTTILA

M 23 Subdoppler Study of the $v_3 = 2$ State of SF_6 by IR-IR Double Resonance with a Sideband Spectrometer
M. KHELKHAL, E. RUSINEK, J. LEGRAND, F. HERLEMONT, AND G. PIERRE

M 24 Measurements of Ultraviolet-Visible Absorption Cross Sections of $BrONO_2$ (Bromine Nitrate)
B. DETERS, J. ORPHAL, AND J.P. BURROWS

M 25 Ambiguity of Coriolis Parameters describing the $2\nu_5/\nu_4$ and $\nu_4+2\nu_5/2\nu_4$ Resonance Systems of HCNO
K. ISLAMI, R. SCHERMAUL, G. SCHULZE, B.P. WINNEWISSER, AND M. WINNEWISSER

M 26 High-Resolution Infrared Study of the ν_3 and ν_4 Fundamentals of $CF_2 = CHF$
R. VISINONI AND S. GIORGIANNI

M 27 Assignment and Analysis of the Rotational Spectrum of CH_2I_2
W. CAMINATI, P. FAVERO, Z. KISIEL, AND L. PSZCZOLKOWSKI

M 28 Infrared Absorption Cross Sections and Band Strengths of HFC-32 Vapour (Difluoromethane)
G. DUXBURY, K. SMITH, D. NEWNHAM, M. PAGE, AND J. BALLARD

M 29 Rotational Spectrum and Internal Rotation Barrier of 1-Chloro-1-Fluoroethane
R. HINZE, A. LESARRI, J.C. LOPEZ, J.L. ALONSO, AND A. GUARNIERI

M 30 The Microwave Spectra of some Unstable Molecules Prepared Using a Pulsed Electric Discharge
B. GATEHOUSE, H.S.P. MÜLLER, AND M.C.L. GERRY

M 31 Microwave Spectrum and Structural Analysis of the Dimer of Pyrrole
G. COLUMBERG AND A. BAUDER

M 32 Pressure Broadening in the $^{13}C^{16}O$ 2-0 Band
S. DREHER, S. VOIGT, J. ORPHAL, AND J.P. BURROWS

M 33 "Soft" and "Hard" Collision Models. Experimental Obvservation of Difference in Spectral Line Shape
A. NADEZHDINSKII

M 34 Self-Broadening Coefficients from FTIR Measurements of H_2O
K.A. KEPPLER, G.CH. MELLAU, S. KLEE, VL.G. TYUTEREV, S.N. MIKHAILENKO, B.P. WINNEWISSER, M. WINNEWISSER, AND K.N. RAO

M 35 Collisional Relaxation of the ν_2 Band of HCN Investigated with a Frequency Stabilized Diode Laser
A. BABAY, V. LEMAIRE, B. LEMOINE, AND F. ROHART

M 36 What Happens in FTS when the Experimental Conditions vary during the Recording time ?
V. DANA, J.Y. MANDIN, AND M.-Y. ALLOUT

M 37 The Infrared Spectrum of the Van der Waals Complex $(CO)_2$
M. HAVENITH, S. KOENIG, G. HILPERT, C. LUBINA, M. SCHERER, H. LINNARTZ, AND M. PETRI

M 38 Pure Rotational Spectrum of HF in Ar gas : line parameters and line profiles
I.M. GRIGORIEV, N.N. FILIPPOV, V.V. MILEVSKI, M.V. TONKOV, J. BOISSOLES, G. MONNIER, AND B. KHALIL

M 39 Subdoppler Spectroscopy with a Tunable Sideband Spectrometer : What's new ?
E. RUSINEK, M. KHELKHAL, F. HERLEMONT, AND J. LEGRAND

M 40 Amplification of Atomic Fields by Stimulated Emission of Atoms
C.J. BORDÉ

M 41 CO_2 Faraday LMR Spectroscopy of Ro-vibrational Transitions of SiC
M. WIENKOOP, P.-C. SCHUMANN, P. MÜRTZ, AND W. URBAN

M 42 Fast Computer Codes based on line-by-line Method for Application in Atmospheric Optics
K.M. FIRSOV, M.YU. KATAEV, A.A. MITSEL, YU.N. PONOMAREV, AND I.V. PTASHNIK

M 43 Assignment of Hot Methane Lines in Comet Shoemaker-Levy 9 Collision Spectra
B.M. DINELLI, S. MILLER, N. ACHILLEOS, J. TENNYSON, M.F. JAGOD, T. OKA, J.C. HILICO, AND T.R. GEBALLE

THURSDAY, SEPTEMBER 14   20:00 – 22:00

POSTER SESSION

N

N 1 Theoretical Long-Range Potential Energy Curves for Diatomic Molecules. Applications to various States of Alkali Dimers
G. HADINGER, S. MAGNIER, AND M. AUBERT-FRÉCON

N 2 FTIR-Spectroscopy applied in the Study of gas phase reaction kinetics using isotopes
J. BLOMQUIST, K. DUNCAN, N.W. LARSEN, F.M. NICOLAISEN, AND T. PEDERSEN

N 3 Scattering Approach to the calculation of Excited States of CaF and BaF
M. ARIF AND CH.J. JUNGEN

N 4 High Resolution Fourier Spectrometry of the $^{14}N_2^+$ Ion for Optical Diagnostics in Air Plasma
F. MICHAUD, F. ROUX, S.P. DAVIS, A-D. NGUYEN, AND C.O. LAUX

N 5 Study of Perturbations observed in the Rydberg $C^1\Sigma^+$ and $E\ ^1\Pi \rightarrow B\ ^1\Sigma^+$ Systems of CO
A. LE FLOCH AND C. AMIOT

N 6 Spectroscopically Determined Born-Oppenheimer and Adiabatic Surfaces for H_3^+
B.M. DINELLI, O.L. POLYANSKY, AND J. TENNYSON

N 7 The $X^1A_{1g}0_0$ and $A^1B_{2u}6^1$ Electronic State Polarizabilities of Free Benzene Molecules
M. OKRUSS, R. MÜLLER, AND A. HESE

N 8 The Electric Dipole Moments in the Vibrationless X^1A' and A^1A' State of 2-fluoronaphthalene
I. RÜCKERT, M. OKRUSS, AND A. HESE

N 9 F.T.Spectroscopy of OCS from 3700 to 4800 cm $^{-1}$ (Selection of a Line poiting Programme)
S. NAIM, A. FAYT, I. DUBOIS, AND H. BREDOHL

N 10 Qualitative Treatment of the first Triad of Vibrational States of the H_2O Molecule
A.V. BURENIN

N 11 Five-dimensional local mode-Fermi resonance model for overtone spectra of ammonia
E. KAUPPI AND L. HALONEN

N 12 The $2\nu_1 + 2\nu_3$ Band of Ozone
A. BARBE AND J.J. PLATEAUX

N 13 The ν_4 Band of NH_3^+
F. KÜHNEMANN, S. JOO, T. OKA, AND R. ESCRIBANO

N 14 The Rovibrational Spectrum of BrCN. A Combined High Resolution Infrared and Millimeterwave Study
M. LE GUENNEC, G. WLODARCZAK, J. DEMAISON, H. BÜRGER, AND O. POLANZ

N 15 How Many Anharmonic Resonances are there in the Water Molecule ?
V.I. STARIKOV AND S.N. MIKHAILENKO

N 16 Photo-Acoustic Measurements of Water Vapor Absorption Coefficient in UV Spectral Region
B.A. TIKHOMIROV, V.O. TROITSKII, V.A. KAPITANOV, G.S. EVTUSHENKO, AND YU.N. PONOMAREV

N 17 Rotational States of Molecules : Spectra and the Underlying Classical Dynamics
S.V. PETROV

N 18 Absolute Line Intensities in the ν_2 Band of $^{12}CH_3$ ^{35}Cl by Diode-Laser Spectroscopy
G. BLANQUET, B. LANCE, J. WALRAND, AND J.P. BOUANICH

N 19 Vibrational Rotational Relaxation of Methane in a Supersonic Jet
D.K. BRONNIKOV, D.V. KALININ, V.D. RUSANOV, J.C. HILICO, AND
YU.G. SELIVANOV

N 20 Rotational and Vibrational Analysis of GeH$_4$, GeH$_3$D and GeHD$_3$ Stretching overtone transitions (V=6, 7 and 8) in the visible range
X-G. WANG, D. PERMOGOROV, A. CAMPARGUE, AND H. BÜRGER

N 21 The Octad of Methane (and associated hot bands)
J.C. HILICO, S. TOUMI, L.R. BROWN, AND A.S. PINE

N 22 High Resolution Spectroscopy of small Aromatic molecules in Supersonic Molecular Beam
M. BECUCCI, G. PIETRAPERZIA, E.R. KERSTEL, AND E. CASTELLUCI

N 23 Laboratory and Atmospheric Spectra of the ClONO$_2\nu_5$ Band around 563 cm^{-1} :
New Quantitative Spectroscopic Measurements of Stratospheric Chlorine Nitrate
J. ORPHAL, D.G. JOHNSON, K. CHANCE, G. GUELACHVILI, K.W. JUCKS,
M. MORILLON-CHAPEY, AND W.A. TRAUB

N 24 The Rotation Spectrum of the Excited Vibrational States of DCOOH and Assignment of Optically Pumped Laser Transitions
O.I. BASKAKOV

N 25 Diode Laser Spectrum of Cis-1,2 Difluoroethylene at 1131 cm^{-1} ; Determination of ground and $v_{10} = 1$ State Parameters
P. STOPPA, S. GIORGIANNI, AND S. GHERSETTI

N 26 Structural Determination of H$_2$SiO using Submillimeter-Wave Spectroscopy
S. BAILLEUX, M. BOGEY, C. DEMUYNCK, J.L. DESTOMBES, B. DELCROIX, AND
A. WALTERS

N 27 Microwave Spectra of Methylpyrrole Complexes with one and two Argon Atoms
S.R. HUBER AND A. BAUDER

N 28 The Microwave Spectrum of 1-Chloro-1,2,2,2- Tetrafluoroethane
A. AGUADO, S. BLANCO, J.C. LOPEZ, AND J.L. ALONSO

N 29 Sideband Spectroscopy in the Visible with a Tunable Modulator
U. HÄRING, W.A. KREINER, G. MAGERL, AND W. SCHUPITA

N 30 The NO Dimer. I - Analysis of the ν_5 Band
A. DKHISSI, A. PERRIN, P. SOULARD, AND N. LACOME

N 31 Investigation of Raman Q Branch Profiles of H_2 Perturbed by N_2. Interpretation in terms of Speed Dependent Broadening and Shifting
P. SINCLAIR, J.P. BERGER, X. MICHAUT, R. SAINT-LOUP, H. BERGER, P. JOUBERT, J. BONAMY, AND D. ROBERT

N 32 Pressure Broadening and Line coupling for various Q Branches of CO_2 in Helium
J. BOISSOLES, F. THIBAULT, AND C. BOULET

N 33 Experimental and theoretical Investigation of the broadening and shifts of spectral lines of SO_2 NO_2 and H_2O
B. SUMPF, O. FLEISCHMANN, V.V. PUSTOGOV, H.-D. KRONFELDT, V.V. LAZAREV, YU.N. PONOMAREV, AND V.N. STROINOVA

N 34 Temperature Dependence of line shift and line Broadening Parameters measured with a tunable diode laser (TDL) Spectrometer
T.Y. WANG, TH. GIESEN, R. SCHIEDER, AND G. WINNEWISSER

N 35 Line-Mixing and Non Linear Density Effects in CO_2-He ν_3 and $3\nu_3$ Infrared Bands up to 1000 Bars
L. OZANNE, C. BRODBECK, N. VAN-THANH, J.P. BOUANICH, J.M. HARTMANN, AND C. BOULET

N 36 Tunable Diode Laser Based Systems for Analytical Applications
A.I. NADEZHDINSKII

N 37 The CN Mode of HCN : A comparative study of the variation of the transition dipole and the Herman-Wallis constants for seven isotopomers and the influence of vibration-rotation interaction
A. MAKI, W. QUAPP, S. KLEE, G. MELLAU, AND S. ALBERT

N 38 Visible Absorption Spectroscopy Using FTS and A Multipass Optics Gas Cell
D. NEWNHAM, M. PAGE, AND J. BALLARD

N 39 Optimisation of an Acoustooptical Device for Heterodyne Analysis
M.E. FAYE, S. KALITE, AND A. DELAHAIGUE

N 40 Infrared Stimulated Emission of O_3 in Inert Matrices
D. JASMIN, V. RADUCU, P. BROSSET, R. DAHOO, B. GAUTHIER-ROY, AND L. ABOUAF-MARGUIN

N 41 Long-Path FTIR Spectroscopy at very Low Temperatures
A.R.W. MCKELLAR

N 42 High Resolution IR Study of the Coriolis coupling between ν_3 and ν_9 in Methylene Chloride
M. SNELS

FRIDAY, SEPTEMBER 15   9:00

INVITED LECTURES
P

P 1 (title unknown)
    P. THADDEUS

P 2 Interferometry and Optics with Laser prepared Atoms
    W. ERTMER

FRIDAY, SEPTEMBER 14   10:30 – 12:30

POSTER SESSION
Q

Q 1 Microwave Spectrum, Conformation, Intramolecular Hydrogen Bonding and Ab Initio Calculations for Ethylene Glycol Vinylether
    K.-M. MARSTOKK AND H. MOLLENDAL

Q 2 The Infrared Spectrum of the AsH Radical in its $X^3\Sigma^-$ State, Recorded by Laser Magnetic Resonance
    K.D. HENSEL, R.A. HUGHES, AND J.M. BROWN

Q 3 The $B^2\Sigma$ Interaction Potential of LiAr Deduced from Laserspectroscopic Data
    R. BRÜHL AND D. ZIMMERMANN

Q 4 The Long-range Potential of the K_2 $X^1\Sigma_g^+$ Electronic State up to 15 $\mathring{A}$
    C. AMIOT, C.E. FELLOWS, AND J. VERGÈS

Q 5 Use of Lennard-Jones-Potentials for Van der Waals Interaction
    D. ZIMMERMANN

Q 6 High Resolution Laser Spectroscopy on the $S_1 \leftarrow S_0 6_0^1$ Vibronic Band of Benzene and Interpretation of the Observed Spectrum
    M. OKRUSS, R. MÜLLER, AND A. HESE

Q 7 Laserspectroscopy on Pentacene Molecules in a Supersonic Jet
    E. HEINECKE, D. HARTMANN, R. MÜLLER, AND A. HESE

Q 8 A Possible Identification of the FeH_2 Radical from its Infrared Spectrum
    H. KÖRSGEN, P. MÜRTZ, K. LIPUS, J.P. TOWLE, J.M. BROWN, AND W. URBAN

Q 9 Effective Rotation-Pseudorotation Hamiltonian for X_3-Type Molecules and trial Analysis of B-X Band Spectrum of Na_3
    N. OHASHI, M. TSUURA, AND J.T. HOUGEN

Q 10 Investigation of Predictional Abilities of Different Forms of Effective Hamiltonians Based on Molecular Hamiltonian in the Principal Axes of Inertia
A.Ya. Tsaune and M.P. Dyachenko

Q 11 Internal Motion Effects in the Microwave Spectrum of OCS Trimer
J.P. Connelly, A. Bauder, A. Chisholm, B.J. Howard, and J.S. Münter

Q 12 Analysis of High Resolution Infrared Spectra of Ozone in the 4600 cm^{-1} Region
S. Mikhailenko, A. Barbe, J.J. Plateaux, and Vl.G. Tyuterev

Q 13 Lineshifts in the ν_3 Band of N_2O and the $1 \leftarrow 0$ Band of CO Induced by Various Perturbers
F. Rachet, M. Margottin, J.P. Bouanich, A. Henry, and A. Valentin

Q 14 Line Intensities for the 10 μm Bands of $^{32}SO_2$
A. Perrin, J.M. Flaud, C. Camy-Peyret, and Ph. Arcas

Q 15 Study of High Temperature Water Vapor by Fourier Transform Spectroscopy of a low Pressure Flame and Comparison with the HITEMP Database
R. Lanquetin, C. Camy-Peyret, and J. Selby

Q 16 Oxygen Isotopic Substitution in $FC\ell O_3$: The Passage from a Symmetric Top to a Quasi- Spherical Top
F. Meguelatti, G. Graner, and K. Burczyk

Q 17 Optical-Optical Double Resouance Polarization Spectroscopy of the $(1)^1\Pi$ State and $(2)^1\Pi$ State of KRb
N. Okada, S. Kasahara, and H. Kato

Q 18 Millimeter Wave Spectrum of As $^{35}Cl_3$ Observation of K=3 Line Splitting and Determination of Arsenic and Chlorine Hyperfine Parameters
G. Cazzoli, G. Cotti, C. Degli Esposti, L. Dore, and J.M. Colmont

Q 19 Fermi Resonances and Local Modes in Stibine : SbH_3. Fourier Interferometric and Laser Photoacoustic overtone Spectra
J. Lummila, T. Lukka, L. Halonen, and H. Bürger

Q 20 The Coriolis Resonating Triad $\nu_4/\nu_{10}/\nu_11$ of CH_3CD_3
G. Nivellini, F. Tullini, and L. Fusina

Q 21 Regular and Oscillatory Parts of the Density of States : Generating Function Approach
D.A. Sadovskii and B.I. Zhilinskii

Q 22 Far Infrared Emission from Stratospheric Hydrogen Peroxide
B. Rebours

Q 23 Rovibrational Analysis of Cyanoacetylene (HCCCN) on the Basis of Millimeter, Infrared and Stark Spectra
L. Mbosei, B. Coveliers, A. Fayt, E. Arié, G. Graner, J. Cosléou, and J. Demaison

Q 24 High Resolution Infrared Spectrum and Analysis of the ν_9 Band of $CH_2 = CHF$
A. GAMBI

Q 25 Diode Laser Spectroscopy of Chlorofluoromethane in the 9-10 μm Region
A. BALDACCI AND P. STOPPA

Q 26 Analysis of the LMR Spectra of CH_2Br
Y. LIU, Z. LIU, AND P.B. DAVIES

Q 27 High Resolution FTIR-Spectra of the Perpendicular Fundamental ν_8 of Trideutero-Triazine
R. RUBER, B. MACHT, AND A. RUOFF

Q 28 The Rotational Stark Effect of Propynyl Isocyanide
J. GRIPP, U. KRETSCHMER, W. STAHL, D. LENTZ, B. MEISNER, N. NICKELT, AND D. PREUGSCHAT

Q 29 Sub-Doppler Zeeman Spectroscopy of the S_1 B_{3u} - S_0 A_{1g} O_0^0 Band of Pyrazine
M. BABA

Q 30 Global fit of Torsional-Rotational Transitions in the $\nu_t = 0$ and 1 Torsional States of Methanol
L.H. XU AND J.T. HOUGEN

Q 31 IR Lineshift Measurements in the $V=2 \leftarrow V = 0$ Band of CO perturbed by He, Kr, N_2 and O_2
J.L. DOMENECH, D. BERMEJO, R. MARTINEZ, J. SANTOS, J.P. BOUANICH, AND C. BOULET

Q 32 Resonance Effects in Molecular Spectra Collision Broadening and Shift
A.I. NADEZHDINSKII

Q 33 Self-, air, nitrogen and noble gas broadening in the ν_1 and ν_3 bands of H_2S
I. MEUSEL, B. SUMPF, AND H.-D. KRONFELDT

Q 34 Line shapes Investigated by coherent transient experiments : narrowing and asymetry induced by the speed dependence of relaxation rates
F. ROHART AND F. KAGHAT

Q 35 Sub-Doppler Line Shapes and Self-Induced Pressure Effects of Calibration Gases CO and OCS at very Low Pressure
M.H. WAPPELHORST, P. PALM, M. MÜRTZ, AND W. URBAN

Q 36 The NO Dimer. II- Analysis of the ν_1 Band
A. DKHISSI, A. PERRIN, AND N. LACOME

Q 37 Intramolecular Vibrations of the Phenol Dimer revealed by Spectral Hole Burning (SHB) and Dispersed Fluorescence Spectroscopy
M. SCHMITT, U. HENRICHS, H. MÜLLER, AND K. KLEINERMANNS

Q 38 Fourier Transform Microwave Spectra of Acetanhybride in a Pulsed Nozzle
Molecular Beam
J.C. GRECU, J. SEBBACH, AND A. BAUDER

Q 39 Spectrometric and Photoacoustic Combined Spectrometer
M.R. DE BACKER, V. ZENINARI, D. COURTOIS, YU.N. PONOMAREV, O.V. TIKHOMIROVA,
AND B.A. TIKHOMOROV

Q 40 Wavenumber Measurements of Molecular Transitions in the 1.2 μm - 1.5 μm Range
by Fourier Transform Spectroscopy
Q. KOU, PH. COUSSON, R. FARRENQ, A. UBELMANN, AND G. GUELACHVILI

Q 41 Photon Echo Study of Molecular collisions
L.S. VASILENKO, N.N. RUBTSOVA, AND E.B. HVOROSTOV

Q 42 Coherent Transient Spectroscopy of High Resolution in Gas
L.S. VASILENKO, N.N. RUBTSOVA, AND E.B. HVOROSTOV

FRIDAY, SEPTEMBER 15   14:00 – 16:00

INVITED LECTURES
R

R 1 Potential Energy Surfaces from the Spectroscopy of Van der Waals Complexes :
closed-shell and open-shell systems
J.M. HUTSON

R 2 Highly Excited Vibrational States of Small Polyatomic Molecules
L. HALONEN

RESUMES

ABSTRACTS

A1

FREQUENCY MEASUREMENTS OF FLUORESCENCE-STABILIZED CO_2 AND N_2O LASERS: ACCURATE MOLECULAR CONSTANTS AND FREQUENCIES

K. M. Evenson
Time and Frequency Division
National Institute of Standards and Technology
Boulder, Colorado, 80303
USA

An ultra-high-resolution low-loss infrared laser oscillating on more than 400 lines of CO_2 or N_2O, provides a radiation source for the extension of frequency measurement to high J regular band lines and lines of other bands of CO_2 [1-4] and N_2O including the 9 micron band to be described in Maki to Maki[5]. These measurements yield new molecular constants and a new set of standard frequencies and wavelengths in the infrared. The laser design and the experimental details will be described, and the results will be presented.

A far-infrared (FIR) spectrometer[6] has been built using the difference frequencies from a pair of fluorescence stabilized CO_2 lasers. This spectrometer provides a tunable source of FIR radiation which is highly accurate for measuring FIR spectra. Highly accurate rotational molecular constants of CO[7] and NO[8] have been measured with this spectrometer, and these measurements will be presented.

1.   K. M. Evenson, Che-Chung Chou, B. W. Bach, and K. G. Bach, IEEE J. Quantum Electron. 30, 1187, 1994.
2.   A. G. Maki, Che-Chung Chou, K. M. Evenson, L. R. Zink, and Jow-Tsong Shy, J. Mol. Spectrosc. 167, 211, 1994.
3.   Che- Chung Chou, K. M. Evenson, L. R. Zink, A. G. Maki, and Jow-Tsong Shy, IEEE J. Quantum Electron. 31, 343, 1995.
4.   Che-Chung Chou, A. G. Maki, S. Ja. Tochitsky, Jow-Tsong Shy, K. M. Evenson, and L. R. Zink, (Frequencies of Sequence Band Lines), J. Mol. Spectrosc., in press.
5.   Maki Tachikawa, K. M. Evenson, L. R. Zink, and A. G. Maki, in preparation.
6.   K. M. Evenson, D. A. Jennings, and M. D. Vanek, in Frontiers of Laser Spectroscopy of Gases, ed. by A.C.D. Alves, pp.43-51, 1988.
7.   T. C. Varberg and K. M. Evenson, Astrophys. J. 385, 763,1992.
8.   F. Stroh, K.M. Evenson, L.R. Zink, and A.G. Maki, in preparation.

A2

INTERMOLECULAR VIBRATIONS OF AROMATIC MOLECULE VAN DER WAALS COMPLEXES : EXACT QUANTUM THEORY AND EXPERIMENT

S. Leutwyler
Institut für Anorganische und Physikalische Chemie
Universität Bern
Freiestrasse 3, 3000-Bern
Switzerland

B1

Lineshape parameters and Q branch shapes for absorption spectra of CH_3F in rare gases.

I. M. Grigoriev,[†] R. Le Doucen, and A. Benidar
Département de Physique Atomique et Moléculaire, URA 1203 du CNRS,
Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France

N. N. Filippov and M. V. Tonkov
Institute of Physics, St.Petersburg University,
Peterhof, 198904 St.Petersburg, Russia

Absorption spectra of CH_3F mixed with He and Ar are recorded by the BRUKER IFS 120 HR spectrometer (Rennes) in the spectral regions $950 - 1250$ and $2850 - 3100$ cm^{-1} with resolution up to 0.002 cm^{-1} at room temperature. The transformation of the shapes of ν_3, ν_6 and ν_4 vibration-rotation bands is investigated with the variation of foreign gas pressure from 25 Torr to 30 bar.

We have estimated the broadening coefficients for the lines of the parallel band ν_3 from lower pressure spectra. Their values depend on J whereas there is no significant difference for the chosen foreign gases. We compare the experimental lineshape parameters with the very recent data for the bands ν_2 and ν_5 of $^{12}CH_3F$ obtained from diode laser measurements[1] and with the data on CH_3Cl available in the literature. The broadening coefficients are about 6 times less than for self-broadening of CH_3F and of the same order of magnitude with those for air broadening. The analysis of intensity distribution in this band for lower pressures is also presented.

The experimental ν_3 bandshapes at higher pressures differ significantly from the model ones calculated as the sum of Lorentz lineshapes. The deviations are more pronounced for the mixtures with He than for those with Ar. These regularities are similar to the case of perpendicular bands of linear molecules for which they were attributed[2] to the line mixing effect.

The slope of the pressure dependence of the apparent Q branch widths of the perpendicular bands at higher pressures is considerably less than the broadening coefficients of isolated lines at lower pressures. This indicates that for the perpendicular bands of symmetric tops the line mixing effect is also essential.

[†]Permanent address: Institute of Physics, St.Petersburg University, Peterhof, 198904 St.Petersburg, Russia.
[1]D. Guerin, M. Nishan, D. Clark, V. Dunjko, and A. W. Mantz, *J.Mol.Spectrosc.* **166**, 130 (1994).
[2]A. B. Dokuchaev, A. Yu. Pavlov, E. N. Stroganova, and M. V. Tonkov, *Opt. Spectrosc.* **60**(5), 585 (1986).

B2

THE POTENTIEL BARRIER OF THE $B^1\Pi_U$ STATE OF Li_2

I. Russier, F. Martin, A.J. Ross, C. Linton[1], P. Crozet, S. Churassy

and R. Bacis

Laboratoire de Spectrométrie Ionique et Moléculaire,

Bât 205 Université Lyon I, Campus de La Doua,

69622 Villeurbanne Cedex, France.

[1]Department of Physics, University of New Brunswick, P.O. Box 4400,

Fredericton New Brunwick, Canada E3B 5A3.

The $F^1\Sigma_g^+$ state of both $^6Li_2$ et $^7Li_2$ has been excited by an optical-optical double resonance scheme $F^1\Sigma_g^+ \leftarrow A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$, and the laser induced fluorescence from $F^1\Sigma_g^+$ recorded on a Fourier transform spectrometer. By using two single mode tunable cw lasers (one sapphire-titanium and the other a ring dye laser) we were able to choose the two steps in order to populate an upper state level (v,J) which gave strong transitions to the highest vibrational levels of $B^1\Pi_u$ in the subsequent $F^1\Sigma_g^+ \rightarrow B^1\Pi_u$ fluorescence.

The $B^1\Pi_u$ state has a potential barrier and the levels near the top of the barrier are broadened by tunneling through the barrier. Our high resolution Fourier transform records have allowed us to position and measure the widths of the broadened lines close to the top of the barrier as a function of v" and J" in the $B^1\Pi_u$ state.

From our data, we have constructed a potential energy curve for the $B^1\Pi_u$ state of $^6Li_2$ and $^7Li_2$ which indicates that the height of the barrier to dissociation is 500 ± 1 cm^{-1}. The shape of the barrier gives linewidths which are consistent with our observations of linewidths varying from 0.04 to 8 cm^{-1} in the quasibound region.

B3

Extended Molecular Symmetry Groups for Systems with Two Coaxial Rotors

Pavel Soldán

J. Heyrovský Institute of Physical Chemistry
Academy of Sciences of the Czech Republic
Dolejškova 3, 182 23 Prague 8
Czech Republic

A general method for constructing molecular symmetry groups and their q-fold extensions of molecules containing two coaxial rotors is developed (cases of identical[1] and non-identical[2] rotors are distinguished). Group structures and character tables are computed, and, for the case of non-identical rotors, general formulas for irreducible representations are also derived. The method is used for symmetry analysis of the H_5^+ and $H_3^+D_2$ complexes (Refs.[3,4]).

[1,2] - P. Soldán: J. Mol. Spectrosc., submitted.

[3] - P. Soldán: J. Mol. Spectrosc. **168**, 258-270 (1994).

[4] - V. Špirko, P. Soldán, and W. P. Kraemer: in preparation.

B4

ROVIBRATIONAL SPECTROSCOPY AND INTRAMOLECULAR DYNAMICS OF ACETYLENE IN THE ELECTRONIC GROUND STATE.

Abbouti Temsamani Mohammed, Michel Herman
Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, Brussels Belgium
and Remy Jost
Laboratoire des Champs magnetiques intenses, CNRS, Grenoble France

Our present contribution is concerned with the use of high resolution molecular spectroscopy and appropriate theoretical approach to understand and to quantitatively describe the ro-vibrational energy pattern of *Acetylene isotopomers* from low to highly excited vibrational levels in the electronic ground state. We have performed an extensive rovibrational analysis and absolute intensity measurement of FTIR gas-phase spectra of C_2HD, C_2D_2 and C_2H_2, from infrared to visible range. We shall focus here on the principal isotopomer. An impressive set of rovibrational studies was achieved for this molecule in the literature, including our work, using various experimental techniques (FT, optoacoustic, SEP, double resonance). Our prime goal was to model all these data by fitting an effective vibrational Hamiltonien. We have collected 122 pure vibrational energies in C_2H_2 up to 12000 cm^{-1} and built the entire vibrational matrix which is block diagonalised. Each block corresponds to a well defined *cluster* of levels, connected by the same set of anharmonic resonances. The 122 input energies are reproduced within a standard deviation of 0.75 cm^{-1} with 35 fitted parameters. Adequate rotational terms, were then introduced, to deal with the *ro*-vibrational clustering of states, to reproduce the observed B_v and the higher order centrifugal distortion that, at the effective stage, hide important information on the rotational couplings. Other tests such as the prediction of intensity features and the *local* rotational perturbations, constituted a decisive support to our model. We also calculated the integrated density of vibrational states for each vibrational symmetry up to the energy validity of the model. We have performed a statistical analysis of the vibrational and ro-vibrational levels. We have also predicted the *IVR* behaviour in absorption and SEP schemes.

B5

Coherent Ion Dip spectroscopy of high lying vibrational states in the

S_0 potential surface of weakly bound molecular clusters

R. Neuhauser, H.J. Neusser

Institut für Physikalische und Theoretische Chemie, TU München,
Lichtenbergstr. 4, D-85748 Garching, Germany

Intense, nearly Fourier transform limited nanosecond laser pulses are used for the investigation of the potential surface of van der Waals complexes of aromatic molecules with noble gas atoms and small molecules. The achieved very narrow linewidth of about 60 MHz yield the possibility to resolve single rotational transitions in Resonance Enhanced Multiphoton Ionization (REMPI) experiments and to exploit special coherent phenomena.

To obtain information about van der Waals modes in the electronic ground state S_0 we make use of the recently developed method of Coherent Ion Dip Spectroscopy (CIS). As the well known STIRAP technique [1] that yields a very high population transfer efficiency in few-level systems, the CIS method makes use of the special population dynamics in few level systems, interacting with two intense Fourier transform limited ns-laser pulses in special time sequences. Using a pulse sequence different from that of population transfer experiments we showed experimentally that a nearly 100% blocking of ionization is possible for rotationally resolved double resonance conditions in aromatic molecules and clusters [2,3]. This leads to 100% deep ion dips in CIS experiments.

New results for the S_0 ground state of the C_6D_6-Ar complex are presented. It is shown that several van der Waals states in the S_0 can be observed that have not been detected in the electronic excited S_1 state. The obtained frequencies can be discussed in terms of 1D quantum mechanical potentials.

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[1] U. Gaubatz, P. Rudecki, S. Schiemann, and K. Bergmann, J. Chem. Phys. 92, 5363 (1990);

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[3] R. Neuhauser, R. Sussmann, and H.J. Neusser, Phys. Rev. Lett. , 74 , 3141 (1995)

B6

THE VIBRATIONAL ENERGY PATTERN IN TRANS 1-2 DICHLOROETHANE

Y. ELYOUSSOUFI, M. HERMAN and J. LIEVIN

Laboratoire de Chimie Physique Moléculaire Cpi 160/09;

Université Libre de Bruxelles,

50, Roosevelt ave., B-1050, Brussels, Belgium.

The infrared spectrum of gaseous 1-2 dichloroethane has been measured in the region (0-11000 cm^{-1}) at meduim resolution using FTIR. Several bands have been observed and assigned in this work. The assignment is supported by extended *ab initio* calculations of the harmonic vibrational frequencies and of the transition moments.

The rotational constants (A, B, C) in the ground state and the shape of the potential energy function governing the internal rotation around the C-C bond have been determined from the calculations.

The band at 1232 cm^{-1} assigned to ν_{16} (CH_2 wag) has been recorded at higher resolution and rotationally analysed using an asymmetric top model. The rotational constants (A, B, C) in the ground and $\nu_{16}=1$ level have been fitted.

B7

Na^{7}Li $1^1\Pi(B)$ Electronic State Λ-doubling Analysis.

C. E. Fellows, R. F. Gutterres
Laboratório de Espectroscopia e Laser,
Instituto de Física,
Universidade Federal Fluminense,
Niterói, RJ, 24020-004, Brasil
A. Dias Tavares Jr.
Departamento de Eletrônica Quântica,
Universidade do Estado do Rio de Janeiro,
Rua São Francisco Xavier, 524,
Maracanã, 20550, RJ, Brasil
C. Amiot, J. Vergès
Laboratoire Aimé Cotton,
CNRS II, Bât. 505, Campus d'Orsay,
91405, Orsay, CEDEX, France.

Λ-doubling for a particular vibrational energy level of the Na^{7}Li $1^1\Pi(B)$ electronic state is here calculated using a simple theory. This $1^1\Pi(B)$ state is strongly perturbed by the $3^1\Sigma^+(C)$ electronic state, as reported in a previous work[1] doing that the Λ-doubling constant can not be obtained by a direct reduction of the difference between e and f levels as a function of $[J(J+1)]$. A comparison between experimental data and values obtained in this simple theory shows reasonable agreement.

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[1]C.E.Fellows, J.Vergès and C.Amiot, J. Chem. Phys. **93**, 6281(1990).

B8

High precision spectroscopy on I_2 in the near infrared

B.Bodermann, H. Knöckel, S. Kremser, E. Tiemann
Institut für Quantenoptik
Universität Hannover
Welfengarten 1
D 30167 Hannover

We report on systematic investigations of the I_2 $B\ 0_u^+$ - $X\ 0_g^+$ system in the wavelength region between 775 nm and 795 nm. The aim of the investigations is the realization of a secondary frequency standard in the near infrared. The new idea is to use the systematics in the energy level structure of the well known iodine molecule, which can be described by only a few molecular parameters, to predict a dense comb of reference frequencies. For that purpose the rovibrational and the hyperfine structure of the I_2 spectrum in the accounted wavelength range has to be investigated with higher resolution and accuracy than reported by other authors to be able to derive molecular parameters with sufficient accuracy. The present experiments were performed using tunable diode lasers with a bandwidth of less than 40 kHz and applying the method of collinear saturation spectroscopy. The lasers can be stabilized to hyperfine transitions and beat frequencies between two such lasers were measured with a typical standard deviation of about 20 kHz. In a first step systematic investigations of the hyperfine structure of the (0-15) band were performed. Measurements of absolute frequencies will be undertaken in cooperation with the Physikalisch-Technische Bundesanstalt (PTB Braunschweig). Experimental results will be presented and the observed vibrational and rotational dependence of the hyperfine structure will be interpreted in terms of simple models.

B9

IONICITY IN LANTHANUM MONOXIDE

Mohammed BENCHEIKH

Laboratoire de Dynamique Moléculaire et Photonique,

URA CNRS n° 779

U.S.T de Lille, UFR de Physique, Bât. P5

59655 Villeneuve d'Ascq Cedex - FRANCE

The LaO molecule has been chosen to test the application of ligand field theory (LFT) to metal monoxides. The test consists of a comparison of closed-shell ligand LFT (CSLLFT) results (in which a $2^+/2^-$ ionic $M^{2+}O^{2-}$ model is *a priori* postulated with a point-charge ligand) against *ab initio* MCSCF-MRCI results (in which no ionicity is assumed *a priori* and an internal structure is allowed for the ligand). The aim of the *ab initio* calculations carried out for this study was to get more insight into the significance of the LFT results. Therefore, the La^{3+} core was replaced by a non-empirical pseudopotential adjusted to match the energy levels of the free La^{2+} atomic ion.

The *ab initio* calculations reveal that the effective (Mulliken) ionicity in LaO is not $La^{2+}O^{2-}$ but quite close to La^+O^-. Despite this, the $(2^+/2^-)$ ionic CSLLFT model leads to the correct orbital occupations in the ground state but this model cannot account for the significant covalency contribution via the nominal $2p\pi$ oxygen orbital. A semi-bonding LFT is developped in order to take into account, at least partially, the covalency in the LaO molecule.

B10

FOURIER TRANSFORM ABSORPTION
SPECTROSCOPY OF THE HERZBERG I BANDS OF O_2

K. Yoshino, J.E. Murray, J.R. Esmond, and W.H. Parkinson
*Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138,
U.S.A.*
and
A.P. Thorne, R.C.M. Learner, and G. Cox
Imperial College of Science, Technology, and Medicine, London, U.K.

Fourier transform spectroscopic measurements of the absorption bands of the Herzberg I system ($A\ ^3\Sigma_u^+ - X\ ^3\Sigma_g^-$) of O_2 have been made in the wavelength region 240-270 nm with resolution of 0.06 cm^{-1}. A stable, bright, line-free, background continum and a means to limt the bandwidth of radiation are required in FTS for a good signal-to-noise ratio. We used a high pressure, Xenon lamp (Hamamatsu 300) as the background source. The bandwidth of the background radiation was limited by means of a double-prism, zero angular, and linear dispersion monochrometer. For weak absorption of the Herzberg I bands, we used a White cell, in which the distance of 2.54 m between the two main mirrors was set and adjusted for 16 double passes of light, making a path length of 81.28 m. We used four different pressures of O_2 in the White cell, 60, 120, 200, and 370 Torr.

Rotational line positions are determined with an accuracy of 0.005 cm^{-1}, and rotational term values are obtained for the vibrational levels, $v = 4 - 11$. Molecular constants of these levels are also obtained. We observed and measured pressure broadening of rotational lines. Precise band oscillator strengths of the (4,0) − (11,0) bands are obtained by direct measurement, and they are significantly higher than the previous experimental values. The rotational line strengths and the branching ratios are also presented for the same bands.

B11

QUANTUM BEAT SPECTROSCOPY OF JET COOLED TRANSIENT SPECIES GENERATED BY A PULSED ELECTRICAL DISCHARGE

I.M. Povey, R.T. Carter, H. Bitto and J.R. Huber

Physikalisch-Chemisches Institut der Universität Zürich,

Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Quantum beat spectroscopy has proven to be a powerful tool for high resolution spectroscopy of stable closed shell molecules. In this poster we present the extension of this technique to transient radicals and their van der Waals complexes. The cold radicals were generated with a pulsed electrical discharge nozzle which provided rotational temperatures of $T_r < 20$ K and collisionless conditions. In conjunction with near Fourier transform limited nanosecond laser pulses clean coherent excitation was achieved.

As model systems we have chosen the radical OD and its van der Waals complex Ar-OD whose $\tilde{A}(^2\Sigma^+) - \tilde{X}(^2\Pi)$ systems are well studied by conventional spectroscopy. For both transients we observed quantum beats due to coherent excitation of hyperfine levels. Furthermore the Zeeman splitting of these beats was measured in magnetic fields up to $B < 20$ G and the lifetimes of the excited states determined. In the case of OD, hyperfine splittings of fine structure levels of rotational states $N \leq 3$ of the $\tilde{A}(v' = 0)$ state were measured and hyperfine parameters determined. Similarly, hyperfine splittings of Ar-OD $\tilde{A}(v' = 3)$ were measured. Their analysis is complicated as the spin-rotation and hyperfine interactions are of the same magnitude.

B12

THE LIGHT RADICALS SH, C_2H, AND CN IN THE 1 THZ REGION

E. Klisch, Th. Klaus, S.P. Belov,
R. Schieder, G. Winnewisser

I. Physikalisches Institut, Universität zu Köln,
D–50937 Köln, Germany

and

E. Herbst

Departments of Physics and Astronomy, The Ohio State University,
Columbus, OH 43210

The Cologne terahertz spectrometer has been used to measure the rotational spectra of open shell molecules such as SH, CN, NO and C_2H. Terahertz spectra of other radicals such as CH_2 are investigated.

The lowest rotational transition $J = \frac{3}{2} \leftarrow \frac{1}{2}$ of SH in the $^2\Pi_{\frac{1}{2}}$ state has been measured at 870 GHz completely resolved in hyperfine structure with the Cologne terahertz spectrometer. The SH radical has been produced by discharging H_2S buffered with He and H_2. Although SH has an inverted $^2\Pi$ state, the $^2\Pi_{\frac{1}{2}}$ state is about 375 cm^{-1} above the $^2\Pi_{\frac{3}{2}}$ state, the $J = \frac{3}{2} \leftarrow \frac{1}{2}$ transition falling into the 350 μm atmospheric window should be detectable with ground based telescopes in hot interstellar sources. In addition the isotopomers ^{34}SH and SD have been detected. SD is of astrophysical interest because its first rotational transition is in the 450 GHz region.

CN has been measured in the frequency region between 560 and 1020 GHz in its $^2\Sigma^+$ ground electronic state and in the excited vibrational states up to v=7. CN was produced in a dc-discharge of methylcyanide, CH_3CN, and molecular nitrogen, N_2. Although no splitting of the CN lines due to hyperfine interaction was observed, our new data fitted together with all others available in the literature give the first proof of a linear progression of b_{F_v}, t_v and eQq_v.

Furthermore for C_2H and NO improved parameters were obtained from measurements in the 1 THz region. Sample spectra will be presented.

B13

THE RENNER-TELLER EFFECT IN THE GROUND STATE OF $CuCl_2$

P. Crozet, A.J. Ross, R. Bacis, J.M. Brown[1] and M.P. Barnes[1]

Laboratoire de Spectrométrie Ionique et Moléculaire,
Bât 205 Université Lyon I, Campus La Doua,
69622 Villeurbanne Cedex, France.

[1]Physical Chemistry Laboratory, Oxford University,
South Parks Rd, Oxford OX1 3QZ, England.

The $^2\Pi_{u\,(3/2)} \leftarrow X\,^2\Pi_{g\,(3/2)}$ electronic transition in $CuCl_2$ has been selectively excited with a tunable single-mode dye laser operating near 16100 cm^{-1}. Fluorescence from the (unidentified) vibrational level of the excited state has been recorded in the 11000-16200 cm^{-1} region at a resolution of about 0.06 cm^{-1} on a Bomem Fourier transform spectrometer. In addition to strong transitions to (v 0 0) and (v 0 2) levels of the ground electronic state, a weaker progression has been observed to (v 2 0) levels of $X\,^2\Pi_{g\,(3/2)}$.

The transition to the $(0\,2^\ell\,0)$ vibronic multiplet occurs around 15900 cm^{-1}. A model based on the effective Hamiltonian of Woodward, Fletcher and Brown[a] has been constructed to calculate the $(0\,2^\ell\,0)$ energies. It reproduces the rotational, Renner-Teller and K-doubling patterns appearing in the spectra of $^{63}Cu^{37}Cl_2$ for rotational lines with $6^1/2 \leq J \leq 80^1/2$ to $\pm\,0.01$ cm^{-1}. Both the Renner-Teller parameters obtained from a non-linear least squares fit are rather large : $\varepsilon = -\,0.43$ and $g_K = 9.9$ cm^{-1}, which suggests that the ground state of $CuCl_2$ undergoes significant vibronic interactions with a $^2\Sigma_u$ state.

[a] Mol. Phys. 62 517-36 (1987) and Mol. Phys. 68 261-2 (1989)

EFFECTS OF MAGNETIC FIELD ON THE $15V$ 31344.9 BAND OF CS_2 STUDIED BY SUB-DOPPLER HIGH-RESOLUTION SPECTROSCOPY

Hajime Katô, Atsushi Doi, and Yoshikazu Taroura

Department of Chemistry, Faculty of Science, Kobe University,

Nada-ku, Kobe 657, Japan

Saburo Nagakura

KAST, KSP East 301, 3-2-1 Sakato, Takatsu, Kawasaki 213, Japan

Effects of an external magnetic field on the excitation spectrum of the $15V$ 31344.9 band of the CS_2 molecule are measured with sub-Doppler resolution. New lines are observed to appear near the $R(2)$ and $P(4)$ lines when a magnetic field is applied. These lines are observed to be composed of five components both for the π-pump and for the σ-pump. From a theoretical analysis, we identify the new lines as transitions to the $^3A_2(A_1-B_1)(v^-;12M)$ levels, which become allowed by Zeeman interaction with the $V^1B_2(v';03M)$ level that is mixed with the $^3A_2(B_2)(v;03M)$ level by spin-orbit interaction. Variations of energy shifts and intensities with the magnetic field strength are explained quantitatively by this analysis. M-dependent perturbation and the quenching of fluorescence are observed. The reason why large Zeeman splittings are observed at many lines in the V system of CS_2 can be attributed to the spin-orbit interaction between the $V^1B_2(v';KJM)$ level and the $^3A_2(B_2)(v;KJM)$ level combined with the rotational and/or the Zeeman interactions between $^3A_2(B_2)(v;KJM)$ level and either $^3A_2(A_1+B_1)(v^0;K\pm1JM)$ or $^3A_2(A_1-B_1)(v^\pm;K\pm1J\pm1M)$ levels which are accidentally close in energy.

B15

OVERTONE SPECTROSCOPY IN NITROUS OXIDE

Alain CAMPARGUE AND Dimitri PERMOGOROV

Laboratoire de Spectrométrie Physique(URA)
Université Joseph Fourier de Grenoble
B.P. 87
39042 Saint-Martin-d'Hères Cedex
France

Mohamed BACH, Jean VANDER AUWERA
and Michel HERMAN

Laboratoire de Chimie Physique Moléculaire
Cpi 160/09
Université libre de Bruxelles
Roosevelt ave., 50
Belgium

Masaaki FUJII

Departement of Chemistry
Waseda University
Ohkubo, Tokyo 169
Japan

The near infrared and visible absorption spectrum of nitrous oxide $^{14}N_2^{16}O$ has been recorded by Fourier Transform Spectroscopy, between 6 500 and 11 000 cm^{-1}, and by Intracavity Laser Absorption, between 11 700 and 15 000 cm^{-1}, Nineteen new bands are observed and, altogether, thirty-four cold and hot bands are rotationally analyzed. The related upper term values, vibrational assignments and principal rotational constants, as well as the relative band intensities are quantitatively discussed in terms of the formation of vibrational clusters, on the basis of the effective Hamiltonian developed by J.L. Teffo, V.I.Perevalov and O.M. Lyulin (Journal of Molecular Spectroscopy 168 (1994) 390).

B16

VIBRATIONAL KINETIC OF OZONE
BY PHOTOACOUSTIC TECHNIQUE

B. PARVITTE*, V. ZENINARI*, D. COURTOIS*,

Yu. N. PONOMAREV**, O.V. TIKHOMIROVA**,

B.A. TIKHOMIROV**

*G.S.M.A., U.A. CNRS D 1434, Faculté des Sciences

BP 347 - 51062 REIMS Cédex - France

** Laboratory of Absorption Atmosheric Spectroscopy, Institute of

Atmospheric Optics of SBRAS, Tomsk 634055 - Russia

Study of the vibrational kinetic of ozone molecules in gas mixtures and in atmospheric air is an actual problem linked with the destruction of the ozone layer.

The technique of measurements of the vibrational-translational relaxation time of the excited molecules with the photoacoustic spectrometer is based on the measurement of the phase shift between the photoacoustic signal and the amplitude modulated excitation radiation.

The photoacoustic spectrometer of the GSMA - Reims -France uses a photoacoustic cell designed in the Institute of Atmospheric Optics of SBRAS - Tomsk - Russia. The excitation is that of a continuous wave $^{12}C^{18}O_2$ isotopic waveguide laser. The output photo-acoustic signal is applied to a phase sensitive detection.

The present paper is devoted to measurements of the vibrational-translational relaxation times τ_{VT} of O_3 (001) molecules colliding with the main molecules and atoms of the atmosphere (N_2, O_2, Ar). The deduced results at room temperature (T = 300 K) are :

$$\tau_{VT} (O_3\text{-}N_2) = (1.79 \pm 0.38) \times 10^{-3} \text{ s torr}$$
$$\tau_{VT} (O_3\text{-}O_2) = (1.35 \pm 0.31) \times 10^{-3} \text{ s torr}$$
$$\tau_{VT} (O_3\text{-}Ar) = (4.53 \pm 0.72) \times 10^{-3} \text{ s torr}.$$

B17

THE H_2S ROTATIONAL SPECTRUM.
SOME EVIDENCE FOR FOURFOLD ENERGY LEVEL CLUSTERING

OLEG L. POLYANSKY, STEFAN KLEE
AND GEORG C. MELLAU

Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany.

JEAN DEMAISON

Laboratoire de Spectroscopie Hertzienne, associé au CNRS, Université de Lille I, P5, F-59655 Villeneuve d'Ascq Cedex, France

PER JENSEN

FB 9 – Theoretische Chemie, Bergische Universität – GH Wuppertal, D-42097 Wuppertal, Germany.

The pure rotational spectrum of hydrogen sulfide was recorded using the BRUKER IFS 120 HR Fourier Transform spectrometer at Giessen. The principal aim of this study was to observe the high-K_a transitions $J_{J,0} \leftarrow J_{J-1,1}$ and $J_{J,1} \leftarrow J_{J-1,2}$. In order to increase the S/N ratio for these intercluster lines, the cell was heated to 140°C. The intercluster transitions have been predicted in the wavenumber region 30–60 cm^{-1}, so in the spectrum analysis, special attention was paid to this interval.

Fourfold clustering of energy levels causes the frequency of the intercluster transitions to increase with J until $J = J_{\text{critical}}$, where it starts decreasing. For H_2S, both effective Hamiltonian predictions and variational calculations predict $J_{\text{critical}} = 15$.

We have observed the $J = 13$, 14 and 15 intercluster transitions with a S/N ratio about 200. Reliable observations of the $J = 16$ and 17 transitions would have provided unambiguous proof of fourfold cluster formation in H_2S. Unfortunately the $J = 16$ transitions are obscured by much stronger and broader lines, and the $J = 17$ transitions could be seen only with a quite low S/N ratio. However, the $J = 17$ line observed in the FTIR spectrum coincides with the prediction from an effective Hamiltonian fit of the data up to $K_a = 15$, and we believe that we see the intercluster transitions of H_2S for $J > J_{\text{critical}}$. The measurement of the lines with $J = 16$ and $J = 17$ by microwave techniques, assisted by frequency predictions from the fit of the new FTIR data to the effective Hamiltonian model, seems to be necessary for establishing the existence of fourfold energy level clusters. We hope to be able to present the results of such measurements at the conference.

B18

The $2\nu_2$ band of HOCl

F. Cavazza, G. Di Lonardo and L. Fusina

Dipartimento di Chimica Fisica e Inorganica, Università di Bologna,

Viale Risorgimento 4, I-40136 BOLOGNA, Italia

The infrared spectrum of HOCl, which seems to play an important role in the ozone cycle in the upper atmosphere, has been recorded with a BOMEM DA3.002 FT instrument in the region between 2300 and 2750 cm^{-1} at a resolution of 0.010 cm^{-1}. A multiple reflection cell with a path length of 7 m was filled up to a total pressure of 13 kPa. About 2000 vibration-rotation transitions for HO^{35}Cl and 750 for HO^{37}Cl , belonging to the first overtone of the bending mode of the molecule, $2\nu_2$, have been measured and analyzed. The band has a hybrid structure, with the perpendicular (B-type) component more intense than the parallel one (A-type).

The analysis of the data was based on the usual Watson-type Hamiltonian in the S reduction and I^r representation. Improved sets of molecular constants derived for the $\nu_2 = 2$ state of both isotopic species reproduce the observed transitions within their experimental accuracy.

B19

STUDY OF COLLISIONAL BROADENING AND SHIFT OF H_2O ABSORPTION LINES USING PHOTO-ACOUSTIC TECHNIQUE

V.A. Kapitanov, V.V. Lazarev,
Yu.N. Ponomarev, B.A. Tikhomirov,
and V.N. Stroinova
Institute of Atmospheric Optics of Siberian
Branch of RAS, 1 Akademicheskii Ave., Tomsk
634055, Russia

Dual-channel photo-acoustic (PA) spectrometers with CW and pulsed lasers serve as efficient instruments for measuring the absorption line contours and contour parameters like half-width and line center shift due to pressure or temperature variations.

In this paper we present a description of design and specification of two dual channel PA spectrometers with a frequency-tunable dye (RG6) and solid state ruby lasers. These spectrometers are applied to study of the broadening and shift of weak H_2O absorption lines in the visible spectral range in mixtures with molecular gases and air.

The results of half-width and shift measurements of more than 30 H_2O absorption lines of 103, 401, and 500 vibrational-rotational bands due to collisions with molecules N_2, O_2, H_2 CO_2, CH_3COCH_3, air are presented and discussed.

The experimental data are compared with calculating ones and used for validation of theory.

The further development of the experimental program is discussed.

B20

ROVIBRATIONAL HAMILTONIAN IN RADAU'S COORDINATES FOR CALCULATION OF THE ROTATIONAL ENERGY IN THE FIRST TRIAD OF THE WATER MOLECULE

L. H. Coudert

Laboratoire de Physique Moléculaire et Applications
Unité Propre du C.N.R.S., Université Pierre et Marie Curie
Tour 13 - Case Courrier 76 - 4 Place Jussieu
F-75252 Paris Cedex 05, France

In the present paper, the somewhat successful treatment[1] developed to calculate the rotational energy of the water molecule in the (000) and (010) vibrational states is modified in order to permit the calculation of the rotational energy in the first triad, *i.e.*, in the (100), (020), and (001) vibrational states, which are coupled by strong Fermi-type and Coriolis-type interactions.

The approach involves writing first the rovibrational zeroth-order Hamiltonian of the molecule with the help of Radau's coordinates r_1, r_2, and θ, since they make it possible to obtain a fairly simple expression for this operator.[2-3] In the next step, the effective Hamiltonian for the interacting (100), (020) and (001) vibrational states is derived. The approximation consists in replacing the two coordinates r_1 and r_2 by their average values in these vibrational states in order to obtain, for each of these state, a four-dimensional Hamiltonian corresponding to the large amplitude bending ν_2 mode and to the overall rotation of the molecule.[1] This second step also allows us to obtain expressions for the Coriolis-type coupling operators. In the last step, using vibrational wavefunctions involving Jacobi polynomials,[1] the matrix of the effective Hamiltonian is set-up and diagonalized, and the rovibrational energy is obtained. In the paper, these three steps will be discussed and preliminary results concerning analyses of the rotational energy for levels belonging to the first triad[4-5] will be reported.

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HIGH-RESOLUTION IR STUDY OF $FC\ell^{18}O_3$: ROVIBRATIONAL ANALYSIS OF THE PERPENDICULAR ν_5 AND ν_6 BANDS

F. MEGUELLATI [1], G. GRANER[1], H. BÜRGER[2]
G. PAWELKE[2] and P. PRACNA[3]

(1) Laboratoire de Physique Moléculaire et Applications, CNRS, Bât. 350, Campus d'Orsay,
F - 91405 ORSAY Cédex, France.
(2) Anorganische Chemie, FB 9, Universität-Gesamthochschule,
D - 42097 WUPPERTAL, Germany.
(3) J. Heyrovský Institute of Physical Chemistry, Dolejškova 3
CZ - 182 23 PRAGUE 8, Czech Republic.

$FC\ell^{18}O_3$ is a prolate symmetric top molecule but very close to a spherical top. Due to the zero nuclear spin of ^{18}O, the statistical weights are 1 and 0 for (A_1A_2) and E rotational levels respectively.

In a recent study (1), only the J dependent ground state parameters were determined in absence of perturbation.

In the present work, isotopically pure samples of $F^{35}C\ell^{18}O_3$ and $F^{37}C\ell^{18}O_3$ were prepared and spectra of each isotopic variety were recorded with a Bruker 120 HR interferometer at room temperature in the ranges of 510-620 cm^{-1} and 360-420 cm^{-1} for the ν_5 and ν_6 bands respectively.

Two kinds of essential interactions were found to be important for these bands : the $\Delta\ell=\Delta k=\pm 2$ and especially the $\Delta\ell=0$, $\Delta k=\pm 3$ for the ν_5 band. This enables us to determine the K dependent ground state parameters A_0 and D_K^0.

A set of accurate spectroscopic constants for the upper states of ν_5 and ν_6 and the r_s structure will be given.

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B22

ROTATIONAL, FINE AND HYPERFINE ANALYSES OF THE (0,0) BAND OF THE $B^2\Sigma - X^2\Sigma$ SYSTEM OF INDIUM MONOXIDE

W. J. Balfour, M. D. Saksena and B. J. Shetty
Department of Chemistry
University of Victoria
B. C. Canada
V8W 3P6

R. F. Barrow, J. M. Brown and I. D. Malcolm
Physical and Theoretical Chemistry Laboratory
South Parks Road
Oxford, England
OX1 3QZ

and

A. M. James and B. Simard
Stacie Institute of Molecular Sciences
NRC, 100 Sussex Drive
Ottowa, Canada
K1A 0R6

The InO molecule has been produced in a molecular beam using a laser vaporization source, and its (0–0) band, near 428.2 nm , has been studied by laser-induced fluorescence at sub-Doppler ($\sim 0.005 \mathrm{cm}^{-1}$) resolution. The spectrum is characterized by impressive nuclear magnetic hyperfine structure due to the ^{115}In nucleus. Analysis of the rotational, fine and hyperfine structure in the band indicate that the transition is of the type $^2\Sigma$(case $b_{\beta S}$) - $^2\Sigma$(case $b_{\beta J}$) in which there is a large hyperfine splitting in the upper state and a predominantly spin-rotation splitting in the lower (ground) state of the molecule.

Derived constants, in cm^{-1}, for the two v=0 levels are as follows:

	$X^2\Sigma^+$	$B^2\Sigma^+$
B_0	0.3265302(50)	0.3174524(55)
γ_0	0.127744(73)	0.031495(73)
b_F	0.041987(13)	0.359455(60)
c	0.01827(40)	−0.00423(20)
eQq_0	−0.0212(15)	

Dispersed fluorescence experiments and photographic emission spectroscopy using microwave excitation, hollow cathode and dc arc sources have been employed to obtain vibrational data.

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B23

HIGH RESOLUTION STUDY OF THE ν_2 BAND OF $CH^{35}Cl_3$

V-M. Horneman, R.Paso, J. Pietilä, and R.Anttila
Department of Physical Sciences, University of Oulu
Linnanmaa, 90570 Finland

The chloroform molecule $CHCl_3$ has small rotational constants and accordingly the structure in the rotation-vibration bands is very dense. There seem to be no such investigation until now on the vibration bands, where the rotational structure had been really resolved. Because of two chlorine isotopes, 35 and 37, there exist four abundant isotopic forms in natural $CHCl_3$. The spectrum of that kind of a mixture of molecules can be expected to be too complicated, and so isotopically pure $CH^{35}Cl_3$ was used. (The authors thank Prof. H.Bürger, Wuppertal, for the sample).

The Fourier transform spectrum in the region 600-800 cm^{-1} was measured by using the Bruker instrument in MAX laboratory in Lund, Sweden. The resolution was near to 0.0010 cm^{-1}. The spectrum covers the fundamental bands ν_2 and ν_5; thus far the former one has been analyzed. In this parallel band more than 3000 lines, with $J_{max} = 100$ and $K_{max} = 56$ were assigned. The rotational structure was well resolved, only the lines with K = 0 - 2 remained as an unresolved peak. The band could be fitted according to a model for an unperturbed symmetric top band although some intensity asymmetry appeared, the R lines were stronger than the P lines. The ground state rotational constants were fixed according to millimeter wave measurements[1]. In the fit of 2850 lines with nine refinable parameters the standard deviation was 0.17 x 10^{-3} cm^{-1}. The following results were obtained: $\nu_0 = 676.643310$ (10) cm^{-1}, $B_2 - B_0 = -0.493903$ (6) x $10^{-3}cm^{-1}$ and $C_2 - C_0 = -0.109899$ (22) x10^{-3} cm^{-1}. Values for the changes of the centrifugal constants D were also obtained.

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B24

HIGH RESOLUTION PHOTOACOUSTIC SPECTRUM OF HCCBr

Olavi Vaittinen and Lauri Halonen

Laboratory of Physical Chemistry, P. O. Box 55 (A. I. Virtasen aukio 1),

FIN-00014 University of Helsinki, Finland

Oliver Polanz and Hans Bürger

FB9-Anorganische Chemie, Universität-Gesamthochschule,

D-42097 Wuppertal, Germany

We have recorded high resolution vibration-rotation spectrum of monobromoacetylene (HCCBr) in the wavenumber region 11500 - 14500 cm^{-1}. The measurements have been carried out with a photoacoustic titanium:sapphire ring laser (Coherent 899-21) spectrometer at a Doppler-limited resolution of about 0.02 cm^{-1}. The most intense band systems, $3v_1+v_2$, $4v_1$, $4v_1+v_5$, and $4v_1+v_3$ have been analyzed rotationally for both isotopic species, $HCC^{79}Br$ and $HCC^{81}Br$. The overtone spectrum of bromoacetylene shows rich fine structure due to the two equally-abundant isotopes of bromine and due to many hot bands from the low-lying v_5 fundamental, and due to ro-vibrational resonances. Altogether, we have found some 20 vibration-rotation bands in the studied band systems for each isotopic species. The anharmonic resonance normal coordinate model[1] which was constructed on the basis of earlier FTIR studies of HCCBr has now been applied to provide labels for the high overtone vibrational states of HCCBr. By using the model, we have been able to assign a great majority of the observed vibrational states. The rotational constants of the states have also been reproduced computationally.

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B25

RAMAN INTENSITIES OF $^{12}CD_4$ IN THE PENTAD REGION

L.Touzani, M.Loëte, B.Lavorel, and G.Millot

Laboratoire de Physique de l'Université de Bourgogne
U.R.A. C.N.R.S. 1796
6 bld Gabriel, 21000 DIJON, FRANCE

The Raman spectrum of $^{12}CD_4$ has been recorded in the spectral range 1963 to 2260 cm^{-1} with the high resolution stimulated Raman technique. Two types of experiments have been used : stimulated Raman gain spectroscopy (SGRS) and inverse Raman spectroscopy (IRS). The resolution of the experiment was about 0.0019 cm^{-1} (HWHM, Gaussian). The pressure of the gas sample was in the range 15 to 60 Torr. The spectrum was sampled in the region of the components of the pentad polyad of $^{12}CD_4$.

The elementary spectra of 1 cm^{-1} width have been analyzed by fitting the line profiles to measure the Raman rovibrational line intensities. All recordings were then intensity calibrated to obtain a set of relative intensities. These data have been analyzed by using a polarisability development previously described [Ref. 1]. The five interacting bands (v_1, v_3, $2v_2$, v_2+v_4, $2v_4$) have been simultaneously analyzed by considering an expansion through the 3rd order of the polarisability. Six polarisability parameters were determined from the 747 experimental data, and the calculated intensities agree with the experimental ones within 12 %. This value is close to the estimated experimental uncertainty (8 %).

To check the validity of our results, simulations in the different regions of the pentad spectrum have been made and compared to recordings of both high resolution stimulated or spontaneous Raman spectra.

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B26

Prediction and Observation of the Stark Effect in the ν_3 band of SiF_4 - Transition Intensities

M.P. Coquard and M. Löete
Laboratoire de Physique de L'Université de Bourgogne,
URA CNRS 1796, Faculté des Sciences,
6 Bd Gabriel, 21000 Dijon, France

A. Ainetschian, and W.A. Kreiner
Abteilung Chemische Physik,
Universität Ulm, Germany

Starting from the description of the usual 2×2 matrix model, we present a more general model (larger matrix) for the Stark effect in XY_4 tetrahedral molecules. Similarly to the expression for the zero-field intensities, an additional model for the Stark intensities is developed. Both models allow us to predict the Stark effect with respect to frequency shifts and intensities of the $M-$components, even in cases where several energy levels are strongly interacting. These calculations can be performed for all tetrahedral (XY_4) molecules, provided we know the electric dipole moment parameters in the states or polyads to be studied.

Using dipole moment parameters obtained from the linear Stark effect, we have predicted frequencies and intensities for SiF_4 IR spectra showing the linear as well as the non linear Stark effect. The predictions are compared with experimental data for the ν_3 band of SiF_4. Saturation spectra of several transitions have been recorded with the sideband spectrometer at Ulm. Within fairly small experimental error limits, the observation agrees with the prediction. Therefore it could be shown that the observed $M-$structure confirms the dipole moment parameters used in the Stark Hamiltonian. Examples of calculated and experimental spectra are given.

B27

Algebraic approach to vibrational spectra of tetrahedral molecules.
First order infrared intensity model

C. Leroy, F. Collin, M. Loëte

Laboratoire de Physique de l'Université de Bourgogne,
Théorie des Systèmes Moléculaires et des Phénomènes Non linéaires,
URA CNRS n° 1796,
Université de Bourgogne, 6 B^{lvd} Gabriel - 21000 Dijon, France

We have proposed an algebraic approach to describe the vibrational stretching modes of polyatomic molecules[1,2].

$$U(5) \supset U(4) \supset K(4) \supset S(4) \approx T_d$$

We have built an Hamiltonian adapted to the so-called local molecules. The standard deviation of our fit indicates the ability of our Hamiltonian to reproduce the observed data.

We extend this approach to the electric dipole moment operator. We suggest a form of this operator adapted to the (n000) local states by combining the strentgh of Lie and molecular groups theory method to the necessity of a compact formulation :

$$M_z^{(F_2)} = \alpha \sum_{n=1}^{N} \left(e^{\beta n\, (n)}T_z^{(F_2)} + {}^{(n)}T_z^{(F_2)} e^{\beta n} \right)$$

This one parameter exponential expression for the dipole function can well reproduce the experimental data of the $0 \to n$ (n=6, 7, 8, 9) transitions for the Silane molecule $^{28}SiH_4$.

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[2] C. Leroy, F. Michelot, *Can. J. Phys.* **72**, 274-289 *(1994)*

B28

HIGH RESOLUTION ABSORPTION SPECTRUM OF NITRYL CHLORIDE, $ClNO_2$ at 793 cm^{-1}

Geoffrey Duxbury and Robert McPheat[†]

Department of Physics and Applied Physics, University of Strathclyde, John Anderson Building, 107 Rottenrow, Glasgow G4 0NG, Scotland.

The ν_2 band of $^{35}ClNO_2$ at 12.6 µm has been studied by high resolution Fourier transform spectroscopy. Assignments have been made for 1423 a-type rotational transitions. The band centre is found to be 792.761 cm^{-1}.

Measurements have also been made of the absorption coefficients of the Q branches of the ^{35}Cl and the ^{37}Cl isotopomers of this band. The peak absorption cefficients measured over a range of temperatures from 298 K to 205 K showed no measureable dependence on temperature. That of the ^{35}Cl isotopomer was measured to be 8.6(1.0)$\times$ 10^{-19} cm^2/molecule and that of the ^{37}Cl isotopomer to be 3.5(1.0)$\times$ 10^{-19} cm^2/molecule.

Simulations of the band structure have been made and show very good agreement with the observed spectrum, allowing most of the hot bands to be identified.

B29

SIMPLE MODELLING OF Q-BRANCH ABSORPTION. PRESSURE, TEMPERATURE, AND PERTURBER DEPENDENCES IN THE $2\nu_6$ Q-BRANCH OF $^{12}CH^{35}ClF_2$

Gh. Blanquet and **J. Walrand**
Laboratoire de Spectroscopie Moléculaire
Facultés Universitaires de Notre-Dame de la Paix
Rue de Bruxelles, 61
B-5000 Namur, Belgium

J.-M. Hartmann and **J.-P. Bouanich**
Laboratoire de Physique Moléculaire et Applications (CNRS UPR136)
Université de Paris Sud (bât. 350)
91405 Orsay Cedex, France.

The simple approach developed previously[1] in order to model absorption by Q-branches is applied to the $2\nu_6$ Q-branch of $^{12}CH^{35}ClF_2$ (HCFC-22). Measurements have been made using a tunable diode laser for pure HCFC-22 and mixtures with N_2 and O_2. The pressures and temperatures investigated, which are suitable for atmospheric applications, range from 0.05 to 1.0 atm and from 200 to 300 K, respectively. It is shown that our model enables satisfactory prediction of both the pressure, temperature, and wavenumber dependences of absorption with eleven effective parameters which have been deduced from measured spectra. Their values are in satisfactory agreement with results from other sources. The model proposed can also accurately predict spectra measured by other authors as well as correctly compute atmospheric transmission.

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1 : "Simple modelling of Q-branch absorption. Theoretical model ..." poster presented by R. Rodrigues et al.

B30

A Software Package for Assignments of Vibration-Rotation Bands of Asymmetric Top Molecules

Š. Urban[1,2] and J. Behrend[1,2]

[1] J. Heyrovský Institute, Dolejškova 3, CZ-182 23 Prague 8, Czech Republic
[2] I. Physikalisches Insitut, Universität Köln, D-50937 Köln, Germany

A package of interactive programs for the assignments of vibration-rotation transitions of asymmetric top molecules to the rotational quantum numbers has been developed. The algorithm of the programs is based on the well known combination differences principle when all the transitions to the same upper level can be simultaneously assigned using the knowledge of the value of their mutual energy differences. The system of programs makes possible to represent either three „Loomis-Wood windows" for different branches or to visualize the corresponding three parts of the experimental spectrum, both mutually related by the combination differences and to switch between these representations. The transitions can be searched in „the spectrum window" and then assigned and stored in the multiple Loomis-Wood diagram.

The input data for the assignment analysis are a table of rotational energies of the lower (e.g. ground) vibrational state, peak list, experimental spectrum (optionally, if the spectrum is not available a simulated spectrum calculated from peak list is used), and a guess of the vibrational band origin are the input data for the assignment procedure. As a result, a sorted list of transition wavenumbers with the correct upper and lower state rotational quantum numbers and with estimated experimental uncertainty is generated as output.

In comparison to an analogous program package for the symmetric top molecules[1] which allows simultaneous processing of only three band branches (P, R, and Q), in the case of asymmetric top, five or more transitions can be mutually checked and it obviously improves the assignment security. The program is especially useful for strongly perturbed bands where the standard assignment procedures break down.

Details of the algorithm as well as examples of spectra analyses will be demonstrated.

[1] Š. Urban and J. Behrend, *XIIIth International Conference on High Resolution Molecular Spectroscopy, Poznań 1994, Poster D3*

B31

THE MM-WAVE ROTATIONAL SPECTRUM OF CBrClF$_2$ (HALON BCF)

E.Białkowska, **Z.Kisiel**, and **L.Pszczółkowski**

Institute of Physics, Polish Academy of Sciences
Al.Lotników 32/46, 02-668 Warszawa, Poland

Bromochlorodifluoromethane (Halon-1211, Halon BCF) has until relatively recently been one of the favoured substances for use as a fire extinguishant. Nevertheless increasing concern over the state of the ozone layer led to its use being discontinued by the Montreal Protocol. Considerable amounts of this substance remain and high resolution spectroscopic information that could be used for its atmospheric monitoring has only recently started becoming available [1]. In that work ground state rotational constants and incomplete quartic centrifugal distortion constants were reported for the four most abundant isotopic species of this molecule, based on assignment of low-J transitions. We presently report the results of extensive measurement and analysis of the rotational spectrum of CBrClF$_2$ up to 330 GHz and J in excess of 100 from studies with our broad-band scanning, BWO-based, source-modulated mm-wave spectrometer.

The spectra were usually recorded in the form of broad-band scans by free-running the BWO and following its frequency by phase-locking to it a K-band klystron. We recorded survey scans contiguous in frequenncy over several GHz, which facilited later, off-line analysis. When increased resolution was desired, selected spectra were also recorded by phase-locking the BWO, through a K-band transfer oscillator, to a 3 GHz synthesizer. The predominatly μ_b-type mm-wave spectrum of CBrClF$_2$ was found to be rich, with few discernible patterns and was not well predicted owing to incomplete quartic constants. *Ab initio* calculation of the force field and of quartic cd. constants was therefore used to assign the spectrum. Measurement of over 200 transitions each for the ^{79}Br^{35}Cl and ^{81}Br^{35}Cl isotopic species allowed determination of complete sets of sextic level centrifugal distortion constants. Incomplete sextic-level constants have also been determined for the weaker ^{79}Br^{37}Cl and ^{81}Br^{37}Cl species. We were able to assign and measure the hitherto unobserved a-type transitions, as well as $^b Q$-type transitions for this molecule. In addition rotational spectra in the lowest excited vibrational state of the ^{35}Cl species, which are comparable in intensity to the ^{37}Cl ground states, have been assigned and spectroscopic constants are reported.

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B32

High Resolution FTIR-Spectra of the Parallel Band ν_{12} of ^{13}C -Triazine

M.Pfeffer and A.Ruoff
Sektion Schwingungsspektroskopie
Univeristät Ulm
Albert-Einstein-Allee 11
89069 Ulm
Germany

V.Typke
Universitätsrechenzentrum
Universität Ulm
Albert-Einstein-Allee 11
89069 Ulm
Germany

The isotopomer $^{13}C_3{}^{14}N_3H_3$ of the symmetric triazine (group $D_{3h}(M)$) has been synthesized with a isotopic purity of more than 97%. Its High Resolution FTIR spectrum has been recorded with the Bruker 120 HR (University of Gießen) in the range of 600 - 1000 cm^{-1} the resolution being about 0.002 cm^{-1}.

About 3000 lines of ν_{12} (located at 732 cm^{-1}) have been assigned. The ground state constants and the excited state constants (up to the H's) will be presented.

A preliminary r_0-structure of symmetric triazine will be given being derived from the B_0's of $^{12}C_3{}^{14}N_3H_3$, $^{12}C_3{}^{14}N_3D_3$, $^{12}C_3{}^{15}N_3H_3$ and $^{13}C_3{}^{14}N_3H_3$.

B33

FOURIER TRANSFORM SPECTRUM AND MORBID CALCULATIONS OF PHOSPHAETHYNE (HCP)

Michael Jung, Markus Mengel

and Manfred Winnewisser

Physikalisch Chemisches Institut

Justus-Liebig-Universität Giessen

Heinrich-Buff-Ring 58

D-35392 Giessen, Germany

The FT-IR spectrum of HCP was measured in the ranges 1100–1900 and 2500–3600 cm^{-1} with a Bruker IFS 120 HR at resolutions of 0.0024 and 0.0046 cm^{-1}, respectively. The spectrum of the stretching vibrations ν_1 and ν_3 which fall in these regions had been measured earlier, but with much lower resolution and sensitivity.[1] The Fermi-resonance induced band $(v_1 v_2{}^{l_2} v_3) = (00^{0e}1) \leftarrow (01^{1e}0)$ and overtone vibration subbands $(02^{0e}0) \leftarrow (000)$, $(03^{1e}0) \leftarrow (01^{1e}0)$ and $(03^{1f}0) \leftarrow (01^{1f}0)$ were observed and analysed. Effective constants including Fermi-resonance parameters for $H^{12}CP$ in 6 excited states and for $H^{13}CP$ in 2 excited states will be presented.

The MORBID[2] program was used to refine a potential surface using rovibrational transitions of HCP taken from our own FT-IR data and from highly excited vibrational states obtained by SEP-spectroscopy.[3] The results of these calculations will also be presented.

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[2] P. JENSEN, *J. Mol. Spectrosc.* **128**, 478–501 (1988).

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B34

THE ν_{10} BAND OF PROPYNE-d_1 WITH THE RESOLUTION OF 0.001 CM^{-1} USING A SYNCHROTRON RADIATION SOURCE

R. Paso, V.-M. Horneman, R. Anttila, A.-M. Tolonen, and S. Alanko
Department of Physical Sciences, University of Oulu, FIN-90570 Oulu,
Finland, email Veli-Matti.Horneman@oulu.fi

A very high resolution spectrum has been measured with a Fourier transform spectrometer using a synchtrotron radiation source. Experimental work has been carried out at MAX-lab in Lund, Sweden, where a Bruker IFS 120-HR Fourier transform infrared spectrometer is connected to the 550 MeV storage ring.

The performance of the synchrotron radiation source in high resolution molecular spectroscopy in far infrared region is evaluated with two measurements both performed with Lund's spectrometer. The lowest fundamental band ν_{10} of propyne-d_1 in the region from 275 to 350 cm^{-1} has been recorded with the ring source. This is compared to our registration of the HCCI ν_5 band [1] in the same region using a glowbar source. In both the measurements the spectral resolution was 0.0010 cm^{-1}.

As far as we know, the propyne-d_1 work is the first one where high resolution vibration-rotation band analysis is based on a spectrum measured using a synchrotron radiation source. Signal-to-noise ratio as high as 70 was obtained with a reasonable scanning time of 15 hours. In the analysis more than 1880 transitions from subbands with KΔK = -10 to +8 were accepted in to the calculations. The standard deviation of the least squares fit with 16 molecular parameters was 0.00010 cm^{-1}.

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B35

FT-MICROWAVE SPECTRUM, LARGE-AMPLITUDE MOTIONS, AND *ab initio* CALCULATIONS FOR N_2O_5

J.-U. Grabow, G.T. Fraser, W.J. Lafferty, R.D. Suenram, F.J. Lovas, and K.K. Irikura
National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

A.M. Andrews
Science and Technology Division, Institute for Defense Analysis, 1801 N. Beauregard Street, Alexandia, VA 22311, USA

J.L. Domenech
Instituto de Estructura de la Materia, CSIC, Serano 119, 28006 Madrid, Spain

The Fourier-transform microwave spectrum of the highly reactive atmospheric reservoir species[1] N_2O_5, recently studied in the mm-wave[2] and extensively studied in the infrared, has been investigated. Our initial spectral searches were guided by the electron-diffraction results[3]. Two *b*-type asymmetric-rotor-like spectra are observed, which fit poorly to a rigid-rotor Hamiltonian. Guided by *ab initio* and dynamical calculations which show a planar configuration is energetically unfavorable, these spectra are assigned to two of the tunneling states of the molecule arising from a geared internal rotation of the two NO_2 groups about their respective C_2 axes. Only 4 of the 10 rotational-tunneling species possible in the G_{16} molecular symmetry group for this non-rigid molecule may be observed. This is due to the presence of the 4 equivalent spin-zero oxygen nuclei, which gives zero statistical weights for all but the A_1^+, A_1^-, B_1^+, and B_1^- rotational-tunneling states. Consistent with the tunneling picture, the nuclear quadrupole hyperfine patterns demonstrate that the two nitrogen nuclei occupy dynamically equivalent positions. The hyperfine analysis further establishes that the two observed tunneling states are of A_1^+ and A_1^- symmetry. Further analysis is being attempted to determine the barrier to internal rotation. Initial results indicate that the internal-rotation potential is less anisotropic than implied by the electron-diffraction analysis.

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B-36

The partially correlated strong collisions model for velocity- and state - changing collisions. Application to Ar-broadened HF rovibrational line shape.

P. JOUBERT and D. ROBERT

Laboratoire de Physique Moléculaire

Université de Franche-Comté, 25030 Besançon Cedex, France.

To describe the line shape asymmetries in the Dicke-narrowing regime, different models are used. The strong collision model is based on the kinetic impact equation. In such a model, three types of collisions are considered : the dephasing ones (D), those changing only the velocity (VC) and those changing both velocity and phase (VCD). Only the two following cases were explicitly considered by Rautian and Sobel'man [S.G. Rautian and I.I. Sobel'man, Sov. Phys. Usp. 9, 701 (1967)] i.e. those where the mechanisms arise in the same collisional events (correlated) or in different ones (uncorrelated). In the recent study of the line shape in Ar broadened HF [A.S. Pine, J. Chem. Phys. 101, 3444 (1994)], small asymmetries have been observed. These asymmetries are not well accounted for models of Rautian and Sobel'man (VCD or VC+D). An empirical model has been proposed by Pine in order to get an accurate fit with experimental results.

We propose a more general approach, also based on the kinetic impact equation, but including the three types of collisions VCD+VC+D. This approach in an extension of the correlated (VCD) and uncorrelated (VC+D) models. This partially correlated strong collisional model leads to a clear physical interpretation of the underlying motional narrowing mechanisms. It allows one to obtain an accurate description of the rovibrational line shapes for HF-Ar for all the measured lines (from P(9) to R(8)).

B37

SELF- BROADENING AND SHIFT OF AMMONIA TRANSITIONS VERSUS TEMPERATURE: THEORY AND EXPERIMENTS

G. Baldacchini, A. Ciucci*, F. D'Amato. M. De Rosa*, F. Pelagalli*
ENEA, Dip. Innovazione, Settore Fisica Applicata
CRE Frascati, C.P. 65, 00044 Frascati, Italy

G. Buffa, O. Tarrini
Dip. Fisica, Università di Pisa
Piazza Torricelli 2, 56100 Pisa, Italy

Width, shape and frequency of molecular spectral lines play a very important role for the assessment of molecular parameters and mutual interactions. In particular, line broadening and frequency shift versus pressure are related to the collisional interactions. and several theories have been developed to describe their mechanism. The Anderson-Tsao-Curnutte (ATC) theory is a semiclassical impact theory which leads to calculation codes whose validity must be verified in order to be used for modeling molecular transitions behaviors in various experimental conditions.

We have performed a complete analysis on several absorption lines of ammonia in the range $815 \div 940$ cm^{-1} belonging to the ν_2 band. having measured self- broadening and shift coefficients versus temperature in the range $190 \div 380$ K. The results of this analysis are discussed in detail. with particular attention to those features which don't agree with either theory or the generally accepted empirical behaviours. For instance. according to a widely accepted empirical low, the broadening coefficients should change linearly in a log-log plot as a function of temperature. while the line aQ(7,1) at $\nu = 937.740$ cm^{-1} does not follow this behavior. The same behavior is generally expected for the shift too. but we have found some nonlinearities and at least one case in which the power law is not valid at all.

*) ENEA guest

B38

Quantum number dependence of the self-broadening coefficients in the ν_1 and ν_3 bands of SO_2

B. Sumpf[*], O. Fleischmann, M. Schöne, A. Kissel[**], H.-D. Kronfeldt

Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1

Straße des 17. Juni 135, 10623 Berlin, Germany

e-mail: tdlas@marie.physik.tu-berlin.de

We present results of our experimental studies concerning the self-broadening in the ν_1 and ν_3 bands of SO_2 applying a tunable diode laser spectrometer. The experiments include 30 lines of the ν_1 band with $5 \leq J'' \leq 44$, $0 \leq K_a'' \leq 23$ and 10 lines of the ν_3 band with $4 \leq J'' \leq 60$, $0 \leq K_a'' \leq 18$.

The dependencies of the broadening coefficient γ on the quantum numbers J'' and K_a'' show a pronounced decrease of γ with increasing J'' and K_a'', respectively. In the ν_1 band we observe that the broadening coefficients do not depend on J'' above a certain K_a'' value but for the ν_3 band we found the opposite situation that γ have the same value for all lines with identical J'' value independent on K_a''. This corresponds qualitatively to earlier theoretical results by Tejwani[1], although the absolute values for the broadening coefficient differ especially for larger quantum numbers. The agreement for small quantum numbers is good.

These results will be accomplished by measurements concerning the temperature dependence of the self-broadening coefficient in the ν_3 band for the lines $(51,13,38) \leftarrow (52,23,39)$ and $(58,2,57) \leftarrow (59,2,58)$, some data on the air and nitrogen broadening and first experiments to determine line shift effects in the ν_3 band.

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B39

THE WATER VAPOR LINESHIFT INVESTIGATIONS AT 5 μ REGION

A. Valentin and F. Rachet
Laboratoire de Physique Moleculaire et Applications, CNRS, UPMC
Tour 13, 4 Place Jussieu, 75005 Paris, France

A. Bykov, N. Lavrent'eva, V. Savel'ev and L. Sinitsa
Institute of Atmospheric Optics, Tomsk, 634055, Russia

Water vapor lineshifts induced by nitrogen pressure have been measured using FT-spectrometer with multi-pass absorption cell at $0.0025\ cm^{-1}$ resolution in $1850 - 2230\ cm^{-1}$ spectral region. The measurements have been carried out from three spectra with 32 meters absorption path: the H_2O pressures being equal to 2, 6 and 5 Torr with nitrogen filling equal respectively to 123 and 201 torr for the last two spectra. A special procedure have been used to minimize the errors connected with the assymetry of the contours because of apparatus effects. The fitting of Voigt contour parameters was used to obtain lineshift parameters. Accuracy of lineshift coefficient determination was better than 1 mk/atm. The lineshift coefficients have been determined for well resolved isolated lines of R-branch of v_2 band with high quantum numbers J up to 18. Their values change from +14.4 to -14.5 mk/atm.

The lineshift coefficients have been calculated using the Anderson method and cut-of-free procedure. The dipole-quadrupole, quadrupole-quadrupole. dipole-hexadecapole and polarizational interactions were included in the calculations. The calculations use the fitted parameter - the mean polarizability of the molecule in the (010) vibrational state. The calculated lineshift coefficients are in satisfactory agreement with the measured ones.

The contributions of different type of intermolecular potentials and their dependences on J value will be discussed.

1. P.W. Anderson, Phys. Rev. 76, 647-661 (1949).
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B40

Fully Complex Implementation of the Robert-Bonamy Formalism:
Halfwidths and Line Shifts of H_2O Broadened by N_2 and O_2

R. Lynch and R. R. Gamache
University of Massachusetts Lowell
Center for Atmospheric Research
450 Aiken Street
Lowell, MA, 01854 USA
and
S. P. Neshyba
Department of Chemistry
University of Puget Sound
Tacoma, WA, 98416 USA

Halfwidths and line shifts of water vapor with both nitrogen and oxygen as the perturbing gases have been calculated using the complex formalism of Robert and Bonamy.[1] The interaction potential was taken as a combination of long range electrostatic and atom-atom terms. Vibrational dependence of the isotropic potential is obtained from the polarizability and dipole moment of water vapor via the induction and dispersion interactions. Techniques were developed to incorporate both the real and imaginary parts of the scattering matrix expansion into the calculation. The effects on both the halfwidth and line shift calculations of including various orders of the atom-atom expansion and the imaginary parts of the scattering matrix expansion were investigated. For a nitrogen perturber the halfwidth and line shift parameters can change by as much as 5% in going from a fourth order to an eighth order expansion of the atom-atom potential. For an oxygen perturber the changes can be 20% or higher. Similar changes are found on including the imaginary parts of the scattering matrix expansion. The effects increased with the angular momentum of the states involved in the transitions. The calculations were compared with measured halfwidths and line shifts and show good agreement.

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B41

ON THE SPECTROSCOPIC EVIDENCES OF (HF)$_n$
ISOMERIC STRUCTURES FORMATION

E. G. Tarakanova

Institute of General and Inorganic Chemistry, Russian Academy of Sciences,

Leninsky prosp. 31, Moscow 117907, Russia

F. Huisken

Max-Planck-Institut für Strömungforschung,

Bunsenstr. 10, D-37073 Göttingen, Germany

Some disagreement has been found recently between the spectroscopic data taken with the use of size-selection technique[1] and *ab initio* calculations[2] of vibrational spectra of (HF)$_n$ clusters. To overcome this difficulty in the present paper the vibrational analysis of a set of (HF)$_n$ isomers ($4 \leq n \leq 8$) has been performed in account for the cooperativity effect. It has been demonstrated that mutual influence of the hydrogen bonds results in substantial dependence of the HF-groups stretching vibrations on the cluster topology. In the clusters built up of a ring plus HF-tail the HF stretching frequencies within a ring can differ up to 150 cm^{-1}. In general the variations of ν_{HF}^{ring} at given polymer size n within considered isomeric structures can be up to 300 cm^{-1}.

Vibrational analysis performed thus far enabled us[3] to assign all the (HF)$_n$ polymers absorption features detected in molecular beams and at equilibrium[1,4]. This assignment is in agreement with previously made size-selection attribution[1]. Low-symmetry branched structures seem to contribute significantly to the measured spectra and these structure can be thought even to dominate over pure cycles at $n \geq 6$.

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B42

LABORATORY UV SPECTROSCOPY APPLIED TO RECENT UV OBSERVATIONS OF THE PLANETS BY SPACECRAFT

J.Ajello, D. Shemansky, I. Kanik, G.James, X. Liu, S. Ahmed and M. Ciocca
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

With the newest generation of high resolution UV imaging space instruments (e. g. Hubble Space Telescope resolving power 10^5, Pluto Fast Flyby) poised to take UV spectra at higher resolution and different spectral regions (e.g. Galileo (400-4300 Å) compared to Voyager (400-1700 Å) the UV emissions of all planets will have been examined in great detail. The inner terrestrial planets have UV airglow and auroral spectra dominated by secondary electron excitation created by solar photoioniaztion, while the outer planets indicate electron impact processes that are driven by energetic magnetosphere interactions and create the UV "electroglow". In response to meet the need for accurate cross sections and optically thin UV emission spectra to model and identify spectroscopic observations of the planets over the past 25 years (Mariner 9 at Mars to Galileo at Jupiter) the Jet Propulsion Laboratory (JPL) has been studying the most abundant atomic and molecular species in the solar system (H, H_2, He, N_2, O_2, CO_2, CO, H_2O, NO, Ar, Ne). The interpretation of high resolution planetary spectra requires a coordinated laboratory study of atoms and molecules in the VUV to determine transition probabilities, cross sections and predissociation yields. JPL has built a high resolution 3M spectrometer (resolving power 67000) to study laboratory UV spectra in the low energy electron range (10-100 eV) characteristic of secondary electron processes in the upper atmosphere. We will review the solar system aeronomy atomic and molecular data base created at JPL and describe the relevant spacecraft observations. Of particular interest are recent studies of the Lyman series of H produced by electron impact on H and H_2. The kinetic energy distribution of H(2p) atoms resulting from electron impact dissociation of H_2 has been measured. The distribution is based on the first measurement of the H Lyman-α (H Lα) emission line Doppler profile. Electron impact dissociation of H_2 is believed to be one of the major mechanisms leading to the observed wide profile from Jupiter aurora by the Hubble Space Telescope. The band strengths of the electron excited N_2 (C $^3\Pi_u$ – B $^3\Pi_g$) second positive system have been measured in the middle ultraviolet. The energy dependence of the (0,0) cross section is reported with analytic shape function for use in model calculations of aurora on the Earth. We report a quantitative measurement of the predissociation fraction $0.15 \pm {}^{.01}_{.045}$ at 300 K in the N_2 c_4' $^1\Sigma_u^+$ – X $^1\Sigma_g^+$ (0,0) band, with an experimental determination of rotational line strengths to be used to understand N_2 EUV emission from Titan, Triton and the Earth. CO is the third most abundant molecule in the Interstellar Medium. High resolution EUV spectra of CO can be used to explain C/ CO abundance from predissociation of the B,C, E states.

B43

FINE STRUCTURE OF INFRARED TRANSITIONS IN SOLID HYDROGEN

R.A. Steinhoff, M. Mengel, B.P. Winnewisser

and M. Winnewisser

Physikalisch Chemisches Institut

Justus-Liebig-Universität Giessen

Heinrich-Buff-Ring 58

D-35392 Giessen, Germany

In recent FT-IR measurements of solid hydrogen using a specially designed multipass cell a number of weak transitions were observed. Among these are satellite structures of the $U_1(0)$ and $U_1(1)$ transitions reported earlier[1]. Their assignment and an intensity calculation based on the theory of Van Kranendonk[2] and Harris et. al.[3] are presented. Furthermore satellite structures of the $Q_2(0)$ and $Q_2(1)$ transitions and the $Q_1(0)$ + $Q_1(1)$ double transition were observed for the first time. Two sharp lines near 8300 cm^{-1} were identified as components of the $Q_1(1)$ + $Q_1(1)$ double transition.

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C1

HIGH RESOLUTION LASER SPECTROSCOPY
IN THE EXTREME ULTRAVIOLET (50-100 NM)

W. Ubachs

Laser Centre, Vrije Universiteit, Amsterdam, Netherlands

A source of narrowband and tunable radiation in the extreme ultraviolet (XUV) wavelength range between 50 and 100 nm, based on the nonlinear upconversion of the powerful output of Nd-YAG pumped pulsed dye lasers, is developed into a versatile tool for atomic and molecular spectroscopy. The bandwidth of the XUV-laser is nearly Fourier-transform limited and superior to synchrotron sources. In a crossed beam configuration sub-Doppler spectroscopy is possible at these short wavelengths. Since exact third and fifth harmonics are generated after frequency doubling the visible output of tunable lasers, an absolute wavelength standard with high accuracy in the XUV is provided via reference to the I_2 and Te_2 standard in the visible.

This narrowband source is applied in studies on:

- the predissociation of carbon monoxide through the measurement of line broadening phenomena.

- a determination of the Lamb shift in the ground state of atomic helium through a measurement of the transition frequency of the ^1S - ^1P transition at 58 nm.

- transitions to autoionizing levels in molecular hydrogen in XUV-near-infrared double resonance studies; these transitions may or may not be the carrier of the "Diffuse Interstellar Bands".

C2

Recent Progress in Internal Rotation : What Happens Above the Barrier?

I. Kleiner

Recently there was a considerable interest in using spectroscopic high resolution techniques to investigate in detail phenomena involving the vibrational quasi-continuum in simple prototype systems. Acetaldehyde, CH_3CHO was chosen for the present work because: 1) methyl groups are thought to be efficient promotors in intramolecular vibrational relaxation (IVR), 2) the internal rotation of the methyl group is a relatively easy one-dimensional large amplitude motion to be described theoretically and 3) the internal rotation is the only very low frequency mode in CH_3CHO and can be thus considered as the only cause of the high density of states.

The talk will be divided into 2 parts:

1) the understanding of the isolated torsional motion below and especially above the torsional barrier top. Microwave and far-infrared data for the 4 lowest torsional levels vt=0,1,2,3 (and a limited number of data in the 5th torsional data vt=4) are now mostly understandable within the framework of a pure torsion-rotation model. In addition to the numerical least-squares fit, we will give a qualitative and more general view of internal rotation phenomena above the barrier involving a theoretical discussion of torsion-rotation interactions above the barrier and showing some sample of intensity calculations. Some of the present difficulties concerning the choice of "good" quantum numbers and the meaning of the traditional K_a K_c labels for rotational energy levels in molecules with internal rotation will be discussed.

2) the understanding of the torsionally mediated interactions in the vibrational manifold. The very dense region from 700 to 950 cm^{-1} corresponding to the two fundamental bands v_{14} and v_9 located at 764 and 867 cm^{-1} respectively and the combination band $v_{14}+v_{15}(=vt)$ at 920 cm^{-1} has been partly assigned. Based on the success of the torsion-rotation model used in 1) and using existing therory a fit has been carried out on the v_{14} isolated band. At the time of this abstract we are attempting to carry out a two-interacting-states global fit of the 867 and 920 cm^{-1} bands which are known to be in a torsionally mediated Fermi resonance.

A FTIR spectra (Brussels and Paris) has been newly recorded for the region of 1100 and 1430 cm^{-1} and analysis of this extremely dense spectra is just beginning. Hopefully preliminary results will be available for the time of the talk.

Recently some of the techniques developed for acetaldehyde turned out to be successful when applied by Dr.L-H. Xu to the related molecule of methanol CH_3OH and I will briefly show an example of this result.

D1

An investigation of the SO molecule by 1+1 REMPI-TOF spectroscopy

C.Braatz, E. Tiemann

Institut für Quantenoptik

Universität Hannover

Welfengarten 1

D 30167 Hannover

The $A^3\Pi$ - $X^3\Sigma^-$ transition of SO was investigated by 1+1 resonance-enhanced multiphoton ionisation (REMPI) with time of flight (TOF) detection. The SO radical was produced by photodissociation of SO_2 in a supersonic jet. With different dissociation energies it is possible to prepare the SO ground state $X^3\Sigma^-$ with different vibrational and rotational population. The 1+1 REMPI-TOF technique allows the first observation of bands with v'= 9 to v'= 14 of the $A^3\Pi$ state. The convergence limit of the vibrational progression give a new interpretation about the dissoziation levels of the $A^3\Pi$, the $C^3\Pi$ and the $X^3\Sigma^-$ state. The analysis of many rotational pertubations has yielded approximate constants for the predicted $C^3\Pi$ state.

D2

HIGH RESOLUTION LASER SPECTROSCOPY OF TiO

C.Amiot, **P.Luc** and **R.Vetter**
Laboratoire Aimé Cotton, C.N.R.S.II, Bât.505, Campus d'Orsay
91405 Orsay Cedex, France

The spectrum of titanium monoxide molecules is of great importance in astrophysics since it is used to calibrate the temperature of cool dwarfs. It has been the subject of many experimental and theoretical studies which, although limited by spectral resolution, have led to the characterization of the lowest singlet and triplet electronic states. Here we present high resolution new results concerning the B $^3\Pi(v'=1)$ - X $^3\Delta(v''=0)$ band in the visible.

The experimental set-up includes an effusive beam of TiO molecules obtained by heating a tungsten crucible at 2200 K and a cw single-mode tunable dye laser operating between 16800 and 17200 cm^{-1}. The two beams cross at right angle and the laser-induced fluorescence technique is used to detect the absorption signal versus the laser frequency. Owing to the reduced Doppler effect, the absorption spectrum consists of narrow lines ($\delta\sigma = 10^{-3}$ cm^{-1}) whose precise calibration is performed by simultaneously recording the iodine molecule absorption spectrum and reference fringes provided by a spherical Fabry-Perot etalon.
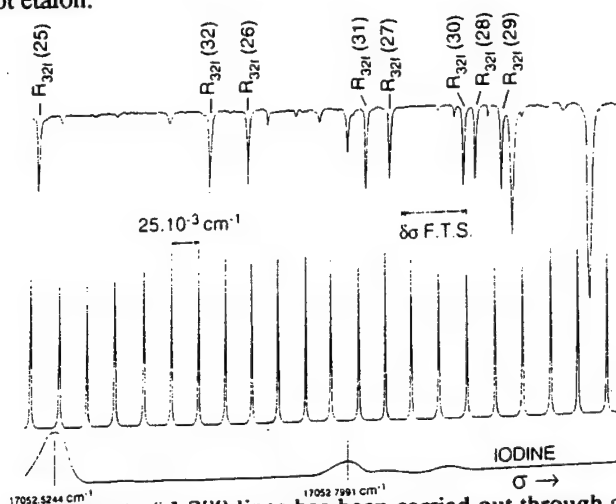
The assignment of 1,200 lines has been carried out through an iterative least-square fit procedure where the wavenumbers are calculated from a case (a) effective Hamiltonian (r.m.s. error = 2 10^{-3} cm^{-1}). The rotational analysis has been extended up to J" = 94 and the spectroscopic data have been reduced to a set of 24 molecular constants among which 8 higher-order ones are determined for the first time. The spin-orbit and Λ-doubling constants for the B $^3\Pi$ state show that the electronic structure in terms of molecular orbitals has to be reconsidered [1].

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D3

FTIR SPECTRUM OF FUNDAMENTAL BAND OF AsO RADICAL

Fumiyuki Ito[*], Taisuke Nakanaga[*] and Harutoshi Takeo[†]

*National Institute of Materials and Chemical Research, Tsukuba, Japan

†National Institute for Advanced Interdisciplinary Research, Tsukuba, Japan

Kay Essig and Harold Jones

Abteilung Chemische Physik, Universität Ulm, Germany

An FTIR spectrum of fundamental band of AsO radical in the electronic ground state $(X^2\Pi_r)$ was measured with an apodized resolution of 0.006 cm^{-1}. The molecule was produced in the same way as used in the diode laser spectroscopy of AsO[1]. About 1000 transitions with v''=0-3, J''<80.5 were assigned and the molecular constants including higher-order corrections to spin-orbit coupling constant were determined with σ=0.0010 cm^{-1}. An r-dependence of the spin-orbit interaction constant A(r) was derived from the higher-order correction terms and was compared with that of PO radical[2].

1) K. Essig, H. Jones, F.Ito and H. Takeo, J. Mol. Spectrosc., 170, 152-157 (1995).

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D4

LASER INDUCED FLUORESCENCE OF THE BLUE-VIOLET
TRANSITIONS OF NiF

C. Dufour and B. Pinchemel

Laboratoire de Dynamique Moléculaire et Photonique

Université de Lille I - UFR de Physique - Bâtiment P5

59655 Villeneuve d'Ascq Cedex, France

Using an improved high density molecular source, it has been possible to record at high resolution the laser induced dispersed fluorescence of the blue-violet transition of NiF (420-470 nm). The rotational analysis confirmed the energy level diagram previously published. A new low lying (252 cm^{-1}) $^2\Sigma$ state has been identified, this state is characterised by a large spin-rotation parameter (γ = -0.952 cm^{-1}). The Ω = 3/2 (2224 cm^{-1}) component of the $^2\Delta$ low lying state has been precisely located. The spin-orbit splitting (1394 cm^{-1}) is in good agreement with the theoretical value (1200 cm^{-1}) expected from a molecular configuration $\sigma^2\pi^4\delta^3$ centered on the 3d^9 atomic shell of the Ni$^+$ ion.

D5

ON THE A $^1\Sigma_u^+$ STATE OF Li$_2$

F. Martin, I. Russier, A.J. Ross, C. Linton, P. Crozet, S. Churassy,
R. Bacis, S. Magnier and M. Frécon.

Laboratoire de Spectrométrie Ionique et Moléculaire,
Bât 205 Université Lyon I, Campus La Doua,
69622 Villeurbanne Cedex, France.

[1] Department of Physics, University of New Brunswick, P.O. Box 4400,
Fredericton New Brunswick, Canada E3B 5A3.

Two tunable dye lasers were used to excite the F $^1\Sigma_g^+$ state of ^{6}Li$_2$ and ^{7}Li$_2$ via the F$^1\Sigma_g^+\leftarrow$A $^1\Sigma_u^+\leftarrow$X $^1\Sigma_g^+$ double resonance. The resulting fluorescence was examined in the 8000 - 17000 cm^{-1} region with a Fourier transform spectrometer. When the excited F$^1\Sigma_g^+$ level was nearly in resonance with an E$^1\Sigma_g^+$ (shelf state) level of the same J value, long vibrational progressions were observed in the infrared, the lower levels of which were identified as high vibrational levels (v>30) of the A $^1\Sigma_u^+$ state. By exciting different vibrational levels of the F state at the J values corresponding to the E-F crossing point we were able to record E$\rightarrow$A and F$\rightarrow$A transitions occurring to $0 \leq v" \leq 84$ in the A $^1\Sigma_u^+$ state. We will present the analysis of these spectra, concentrating on the ^{6}Li$_2$ isotopomer.

The highest observed vibrational level of the A $^1\Sigma_u^+$ state in ^{6}Li$_2$, v=84, is located 2.5 cm^{-1} below the 2s (^{2}S$_{1/2}$) + 2p (^{2}P$_{1/2}$) dissociation limit of the lithium dimer. We determine the dissociation energy of the A state to be 9352.2(1) cm^{-1}, and predict the last bound level of A $^1\Sigma_u^+$ in ^{6}Li$_2$ to be v=109. The leading term in the multipolar expansion describing the interaction between Li(2s) and Li(2p) is C$_3$ = 3.58(1) 10^5 cm^{-1} Å^3. The experimental RKR curve extends beyond 35 Å and is compared with a theoretical curve for R $\geq$ 9Å derived from a long range model.

D6

LOW-LYING ELECTRONIC STATES OF ScCl

F. Taher[1], J. Vergès[2], C. Effantin[1], A. Bernard[3],
J. d' Incan[1], and E. A. Shenyavskaya[4]

[1] *Laboratoire de Spectrométrie Ionique et Moléculaire, Université Claude Bernard, Lyon I, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France*
[2] *Laboratoire Aimé Cotton, CNRS II, 91405 Orsay, France* [3] *Observatoire de Lyon, 69561 Saint-Genis-Laval, France* [4] *Thermocentre of the Russian Academy of Sciences, Institute for High Temperatures, Izorskaya 13/19 Moscow 127412, Russia*

Electronic transitions of $^{45}Sc^{35}Cl$ and $^{45}Sc^{37}Cl$ were observed in emission and spectra were recorded with a Fourier transform spectrometer. The $C(2)^1\Sigma^+$, $B(1)^1\Pi \rightarrow X^1\Sigma^+$ and $(2)^3\Delta$, $(1)^3\Phi \rightarrow a^3\Delta$ transitions readily appeared in the thermal emission at 1500 K. The $(2)^3\Delta \rightarrow a^3\Delta(0-0)$ transition was also observed in the fluorescence induced by titanium sapphyre laser lines. The Ar^+ laser lines 476.5 and 457.9 nm were found to excite $(3)^1\Pi(v=0, 1)$ levels, inducing fluorescent transitions to $B(1)^1\Pi$, $c(1)^3\Sigma^+$, $b(1)^3\Pi_0$, and $a^3\Delta$ (the line 476.5 nm also excites $(3)^1\Sigma^+(v=0)$, inducing fluorescence to $B(1)^1\Pi$). It was found that the rotational perturbations observed in $B(1)^1\Pi(v=0$ to 4) levels are caused by $c^3\Sigma^+(v=2$ to 6).

Principal molecular constants (cm^{-1}) of the states, for $^{45}Sc^{35}Cl$, are:

State	T_0	ω_e	B_0	$10^4\alpha_e$
$X^1\Sigma^+$	0	447.50	0.171873	8.66
$a(1)^3\Delta_1$	882	398.3	0.15776	
$a(1)^3\Delta_2$	a	398.3	0.15848	
$\underline{b(1)^3\Pi_0}$	3430	382	0.155	
$\underline{c(1)^3\Sigma^+}$	(5345)	(369)	(0.155)	
$\underline{B(1)^1\Pi}$	5987.74	381.775	0.154722	7.87
$\underline{C(2)^1\Sigma^+}$	12392.54	373.9	0.1574	9.8
$(1)^3\Phi_3$	12564.37+a		0.15095	
$(2)^3\Delta_2$	13088.60+a	355.9	0.15189	
$(3)^1\Pi$	21482.10	373.1	0.15631	8.7
$\underline{(3)^1\Sigma^+}$	(22431.6)	(367.6)	(0.1519)	

Notes: The hitherto unobserved states are underlined. The values of the centrifugal distortion constants are about 10^{-7} cm^{-1}.

D7

ELECTRONIC ABSORPTION SPECTRA OF CARBON CHAINS IN NEON MATRICES. C_{2n}^-, C_{2n}, $C_{2n}H$, $HC_{2n+1}H$, AND C_{2n+1}

Jan Fulara[1], Daniel Forney, Patrick Freivogel, and John P. Maier

Institut für Physikalische Chemie der Universität Basel,

Klingelbergstrasse 80, CH-4056 Basel, Switzerland

Absorption spectra of species isolated in neon matrices have been obtained for the following electronic transitions: C_{2n}^- $^2\Pi \leftarrow X\ ^2\Pi$ (n=2–10), C_{2n} $^3\Sigma_u^- \leftarrow X\ ^3\Sigma_g^-$ (n=3–7), $C_{2n}H$ $^2\Pi \leftarrow X\ ^2\Pi$ (n=3–8), $HC_{2n+1}H$ $^3\Sigma_u^- \leftarrow X\ ^3\Sigma_g^-$ (n=2–7), and C_{2n+1} $^1\Sigma_u^+ \leftarrow X\ ^1\Sigma_g^+$ (n=3–6).

Almost all of these spectra could be recorded after co-deposition of neon with mass selected cations $C_nH_m^+$ (m=0–3) produced in a hot cathode ion source from a 1:1 mixture of diacetylene and helium. Within a homologous series the 0_0^0 bands are shifted in the wavelength spectrum as a function of size. The combination of mass selection and this spectroscopic observation is used to determine the number of carbon atoms of the absorbing species. This procedure already has been reported for polyacetylene[2] and cyanopolyacetylene cations[3].

In order to determine the number of hydrogen atoms and the charge of the carriers, another three preparation techniques have been used: hot cathode anion source, negative ion sputter source and laser vaporisation. Deuteration, photo-bleaching and co-deposition with electron donors and scavengers assisted the assignment.

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[1] Present address: Instytut Fizyki Polskiej Akademii Nauk, Al. Lotników 32-46, 02-668 Warszawa, Poland.

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D8

HIGH RESOLUTION SPECTROSCOPY OF
THE WULF BANDS OF OZONE

A.J. Bouvier, B. Bussery, R. Bacis, S. Churassy, D. Inard, M. Nota,
J. Brion*, J. Charbonnier* and J. Malicet*

*Université Claude Bernard, Lyon I, Laboratoire de Spectrométrie Ionique et
Moléculaire, URA 171 du CNRS, 43 Bd du 11 Novembre 1918, 69622,
Villeurbanne Cedex FRANCE.*
**Laboratoire de Chimie-Physique, Faculté des Sciences de Reims,
FRANCE, BP 347-51062.*

High resolution spectra of the Wulf Bands of ozone have been recorded
in the range 8600-10500 cm^{-1} at two temperatures 23.5°C and -50.8°C with
an instrumental resolution of 0.05 cm^{-1} and an effective resolution of 0.07-
0.08 cm^{-1}. Rovibrational structure have been obtained for three bands, one of
them (hot band) disappearing at low temperature.

The different possible transitions have been simulated using a simple
model based on a slightly asymmetric top representation, accurate data relative
to the ground state and recent ab initio geometrical parameters for the upper
electronic states concerned. The main features of the observed band shapes are
obtained with a transition of $B_1 \leftarrow A_1$ type (with C_{2v} geometry).
Identification and assignments of some well separated bandheads allowed to
determine geometrical parameters and origins of the bands which are
characteristics of the $^3A_2$ state. However the complexity of the rotational
structure indicates that a pure triplet-singlet transition cannot completely
explain the spectrum and we have to consider a mixing of states, perhaps with
$^3B_1$. From the extremely small absorption cross sections we infer a lifetime
at the maximum of the order of several seconds which shows that the excited
state involved is metastable. The origin of the two vibrational levels (0 and 1
bending modes) are separa ted by 531 cm^{-1}. The interactions of this bound
metastable state might have an important role in the ozone cycle models.

THE ν_2 BAND OF HOCl

D. Hurtmans, J. Vander Auwera,

Laboratoire de Chimie Physique Moléculaire C.P. 160/09
Université Libre de Bruxelles
50 avenue F. D. Roosevelt, 1050 Brussels, Belgium

J.-M. Flaud,

Laboratoire de Physique Moléculaire et Applications - CNRS
Université Pierre et Marie Curie
75252 Paris Cedex 05, France

and W. J. Lafferty

Molecular Physics Division
National Institute of Standards and Technology,
Gaithersburg, MA 20899, USA

The main challenge encountered when measuring absolute intensities for hypochlorous acid is determining the partial pressure of this species in the sample since HOCl exists only in equilibrium with H_2O and Cl_2O. Until now, studies dealing with intensity measurements of this molecule have relied on the equilibrium constant determined by other techniques. However, in this work we have used known line intensities of the pure rotational spectrum of HOCl determined from Stark effect measurements to obtain the concentration of this species in the sample mixture.

We have thus designed a thermostatic cell that allows the recording of the far infrared and the infrared spectra of the same sample of hypochlorous acid and that fits into the sample chamber of a Bruker IFS120HR spectrometer. The pure rotation spectrum was recorded between 30 and 240 cm^{-1} using a maximum optical path difference (MOPD) of 300 cm and the ν_2 band of HOCl was recorded between 550 and 2000 cm^{-1} with a MOPD of 180 cm. About 136 and 70 intensities of well isolated lines were measured in the ν_2 band of $HO^{35}Cl$ and $HO^{37}Cl$ respectively.

In order to calculate intensities, one must know precisely the wavefunctions. As noted previously[1], the $K_a = 5$ levels of the $HO^{35}Cl$ molecule are perturbed by $K_a = 4$ levels of the 002 vibrational state. A calculation taking this interaction into account was performed allowing one to locate a few lines of the $2\nu_3$ band as well as to calculate the (010) rotational levels to within their experimental accuracy. Finally experimental intensities were calculated, and a precise transition moment operator for ν_2 was obtained.

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D10

THE ROTATIONAL SPECTRUM IN THE VIBRATIONAL GROUND STATE OF H_2Te

I. N. KOZIN

Applied Physics Institute, Russian Academy of Science,
Uljanov Street 46, 603600 Nizhnii Novgorod, Russia.

S. KLEE

Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen,
Heinrich-Buff-Ring 58, D-35392 Giessen, Germany.

O. POLANZ AND PER JENSEN

FB 9 – Chemie, Bergische Universität – Gesamthochschule Wuppertal,
D-42097 Wuppertal, Germany.

We report here a new high resolution FTIR investigation of the pure rotational spectrum of the H_2Te molecule. The spectra were recorded in the region 30–360 cm^{-1} at temperatures between $-40°C$ and $-30°C$ with a Bruker IFS 120 HR interferometer. Analyses of the pure rotational spectra in the vibrational ground states of the different tellurium-substituted isotopomers have been carried out using an effective Hamiltonian model. Significantly improved molecular parameters have been obtained.

One important aim of the present work is the study of the "cluster effect" (i.e., the formation of nearly degenerate, four-member groups of rotation-vibration energy levels at high rotational excitation) in the vibrational ground state of H_2Te. This effect has been experimentally verified for the vibrational ground state of H_2Se[1]. It has been calculated *ab initio*[2] that in the vibrational ground state of H_2Te, the four highest energy levels at each J value will start to converge towards forming a cluster at $J \approx 12$. Because of the instability of H_2Te which necessitates that spectra be recorded at relatively low temperatures, it is difficult to observe transitions involving the cluster states. In the present investigation we have assigned transitions with $J > 20$. However, the highest K_a value, for which lines could be assigned, was 16. At this K_a value, we have not obtained the "coverage" of the cluster states previously obtained for the H_2Se molecule[1]. However we believe that the present study gives a good starting point for further investigations of cluster phenomena in H_2Te.

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D11

TEMPERATURE DEPENDENCE, IN THE 200-300 K RANGE, OF VIBRATIONAL ENERGY TRANSFERS IN OZONE EXCITED IN THE {(200), (101), (002)} TRIAD.

F. Ménard-Bourcin, L. Doyennette, J. Ménard, <u>C. Boursier</u> and C. Boulet

Laboratoire de Physique Moléculaire et Applications

Unité propre du CNRS, associée aux Universités Paris VI et Paris XI

Université Pierre et Marie Curie, Tour 13, case 76

4. place Jussieu, 75252 Paris Cedex 05, France

From double resonance measurements in O_3-O_2/N_2 mixtures, the relaxation pathway from the triad, was established. As long as the O_3 molar fraction is higher than a few percent, the vibrational deexcitation from the triad occurs first through fast near-resonant V-V transfer processes. The rate coefficients of these transfer processes have been measured, then calculated by means of a semi-classical model. The experimental temperature dependences are well reproduced by the calculations.

From measurements performed with very small O_3 molar fractions, we have shown that the vibrational energy located in the stretching modes relaxes essentially through far from resonance transfers to the v_2 mode rather than simple cascading in the stretching mode.

D12

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF C_3 : THE RENNER EFFECT IN THE ã $^3\Pi_u$ AND b̃ $^3\Pi_g$ ELECTRONICS STATES

S. Civiš,

J. Heyrovský Institute of Physical Chemistry , Czech Academy of Sciences,

18223 Prague 8, Dolejškova 3, Czech Republic

D.W.Tokaryk and G. Herzberg

Steacie Institute for Molecular Sciences, National Research Council of

Canada, Ottawa, Canada, K1A 0R6

We describe the construction of a liquid nitrogen-cooled multireflection emission discharge cell. A combination of very small gas input apertures , and very rapid evacuation through a combination of mechanical and booster pumps, provides for a rapid replenishment of discharge- formed material in the cell. This cell is an excellent source for the study of the C_3 radical in the triplet manifold of the electronics states.

Five new triplet bands of $^{12}C_3$, and three corresponding bands of $^{13}C_3$, have been observed in emission between 6000 cm^{-1} and 6600 cm^{-1} with a Fourier transform spectrometer. Rotational analysis shows that these bands arise from excited bending vibrations of ã $^3\Pi_u \rightarrow$ b̃ $^3\Pi_g$ electronic transition , and that all components of the (010) vibrational level of the b̃ $^3\Pi_g$ state exhibit unusual perturbations. Renner parameters for both electronic states have been extracted from an analysis of the spin-orbit parameters of the (000) $^3\Pi$, (010) $^3\Delta$, (020) $^3\Phi$, and (030) $^3\Gamma$ levels. The Renner effect is shown to be large in both electronic states ($e' = +0.447$, $e'' = +0.566$). Approximate bending vibrational frequencies are also obtained ($\omega' \sim 345$ cm^{-1}, $\omega'' \sim 505$ cm^{-1}).

D13

SIMPLE MODELLING OF Q-BRANCH ABSORPTION.
THEORETICAL MODEL AND APPLICATION TO CO_2 AND N_2O.

R. Rodrigues, J.M. Hartmann, C. Boulet, M. Margottin-Maclou, and F. Rachet
Laboratoire de Physique Moléculaire et Applications (CNRS UPR136)
Campus d'Orsay (bât. 350)
91405 Orsay Cedex, France.

B. Khalil, F. Thibault, and J. Boissoles
Département de Physique Atomique et Moléculaire (CNRS URA 1203)
Université de Rennes I
Campus de Beaulieu
35042 Rennes Cedex, France.

A simple theoretical approach of Q-branch absorption is developed. It is based on the classical approximation of the rotational distribution and a Strong-Collision-type modelling of line-coupling coefficients. The Q-branch absorption is then represented by a very simple analytical expression which depends on six average parameters; pressure and wavenumber dependences are included in the model so that the parameters only depend on the molecular system (active molecule+perturber), band, and temperature. Tests show that, provided effective parameters are used, our model enables very satisfactory predictions of the pressure, temperature, and wavenumber dependences of Q-branch absorption. These effective parameters can be deduced from experimental spectra and no previous knowledge of neither the spectroscopic nor collision parameters is required. This makes the present approach suitable for species[1] (most of those of atmospheric interest) for which no alternative and more accurate approach is yet available.

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1 See poste "Simple modelling of Q-branch absorption. Pressure, Temperature, ..." by Gh. Blanquet et al.

D14

$H_2{}^{18}O$ ABSORPTION SPECTRA BETWEEN 9600 AND 16000 CM^{-1}

J.-M. Flaud, C. Camy-Peyret, J.-Y. Mandin
Universite Pierre et Marie Curie, Paris, 75230 France

A.Bykov,O.Naumenko, T.Petrova, L.Sinitsa and A.Scherbakov
Institute of Atmospheric Optics, Tomsk, 634055, Russia

The spectrum of ^{18}O-enriched water vapor has been recorded between 9000 and 16000 cm^{-1} using Fourier- transform spectrometer with resolution 0.01 cm^{-1} and optical path length 434 m. The positions of more then 4350 lines have been measured with accuracy 0.0001 cm^{-1} for strong lines and 0.005 cm^{-1} for weak lines.

During the assignment procedure the lines of 22 bands and energy levels of highly excited vibrational states which belong to the first, second decades and first and second pentadecades of $H_2{}^{18}O$ have been determined.

Table. Investigated vibrational states.

$3v$	$3v+\delta$	$4v$	$4v+\delta$
(121), (201), (003), (300),	(131), (211), (013)	(301)	(023)
(041), (220), (041), (220),	(310), (051), (230)	(400)	
(022), (102), (140)	(112), (032), (070)	(103)	

In the energy level calculation we should take into account the following:

1. Strong bending- rotation coupling leads to divergence of Watson-type effective rotational Hamiltonian for vibrational states with high v_2 values even at moderate values of rotational quantum numbers K_a. For this reason we used the Pade-Borel approximate method.[1]

2. The vibrational states (070) and (160),(080) have been added to the first and second polyads respectively to explain the perturbations due to HEL- resonances[2,3] in highly excited vibrational states.

Rotational, centrifugal distortion and resonance coupling constants have been determined.

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D15

HIGH RESOLUTION STUDY OF THE IR SPECTRUM OF THE PF$_3$ MOLECULE BETWEEN 645 AND 730 cm^{-1}

M. BADAOUI [1], N. BEN SARI-ZIZI [1], H. NAJIB [1] and G. GRANER [2]

(1)Laboratoire de Spectronomie Physique Appliquée, Faculté des Scoiences,

Université Mohammed V, B.P. 1014, RABAT, Agdal, Maroc.

(2)Laboratoire de Physique Moléculaire et Applications, CNRS, Bât. 350, Campus d'Orsay,

F - 91405 ORSAY Cédex, France.

This range has been recorded at Wuppertal on the Bruker Interferometer of H. BÜRGER with a resolution of 0.003 cm^{-1}. The spectrum contains essentially the parallel component $2v_4^0$ (692.85 cm^{-1}) of the overtone band and the hot band $3v_4^{\pm1}$ - $v_4^{\pm1}$ (691.98 cm^{-1}). These bands have been previously studied[1] at a resolution of 0.05 cm^{-1} but without any rotational structure analysed.

The Q region of $2v_4^0$ is very congested. The P and R sides are characterized by J clusters with a K structure degraded to small wavenumbers. The assignments up to J=53 and K=53 were helped by the pronounced intensity enhancement for K=3p lines and by the use of accurate GSCD's. For this band, 1172 transitions were fitted in a model taking into account the $\ell(2,2)$ interaction between $v_4 = 2$, $\ell=0$ and $v_4 = 2$, $\ell=\pm2$, although no transition of the $2v_4^{\pm2}$ component has been assigned. A s.d. of 0.25 x 10^{-3} cm^{-1} is achieved when we let free the band center of this unknown component.

The component $3v_4^{\pm1}$ - $v_4^{\pm1}$ of the hot band displays two largely separate parts for $\ell=-1$ and $\ell=+1$, the first one being stronger than the second one, with a clear intensity enhancement for K-ℓ=3p. Assignments (up to J=47 and K=18) were made possible by the automatic assignment program Touthot, using LSCD's in the v_4=1 state, derived from the previous study[2] of v_4 . A total of 498 lines (405 for ℓ=-1 and 93 for ℓ=+1) were then fitted according to a model taking into account the $\ell(2,2)$ interaction between $v_4 = 3$, $\ell=\pm1$ and $v_4 = 3$, $\ell=\pm3$, although no transition reaching this level has been assigned. A s.d. of 0.25 x 10^{-3} cm^{-1} is achieved with the band center of $3v_4^{\pm3}$ - $v_4^{\pm1}$ constrained.

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D16

The Microwave Spectrum of IN₃

H.-O. Munz, H.-K. Bodenseh
and
T. M. Klapötke*
Universität Ulm, Abteilung Chemische Physik
Albert-Einstein-Allee 11
D-89069 Ulm
* Chemistry Department, University of Glasgow

The highly explosive iodine azide (IN₃) has been prepared first according to [1], later by a modified procedure more suited for microwave spectrocopy. Since the vapor pressure was sufficient, the rotational spectrum was measured between 10 and 40 GHz and partially assigned.
First results are given.

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D17

ASSIGNMENT OF METHYL CYANIDE FAR INFRARED LASER LINES

H. Sarkkinen, J. Pietilä, R. Paso, and R. Anttila

Department of Physical Sciences, University of Oulu

Linnanmaa, 90570 Oulu, Finland

Methyl cyanide CH_3CN as well as its fully deuterated isotopomer CD_3CN have fundamental bands coincident with the 10.4 or 9.6 μm CO_2 bands and so they are good candidates for FIR laser action. A review of the observed CH_3CN far-infrared laser lines has been given by Inguscio[1]. His article includes observations of 32 laser lines and for most of them some assignment has also been given. For the deuterated species the review includes three laser emissions only. Some years ago Gastaud et al.[2] extended the observations for this molecule by giving a list of 13 transitions.

Recently in our laboratory studies on the infrared spectrum of methyl cyanide, both of CH_3CN as well as of CD_3CN have been carried out. One investigation[3] concerns the FTIR spectrum of CH_3CN between 850 and 1150 cm^{-1}, just the region, where the pumping transitions of the FIR laser lines are located. Some analyses of hot band lines were also performed and they are important in the laser line assignment. In the case of CD_3CN we have measured the spectrum between 900 and 1200 cm^{-1}. More than 5000 lines have been assigned to the fundamentals and to hot bands. As we have still analyzed the lowest fundamental bands of both the molecules we decided to try to improve far-infrared laser line assignments and we also wanted to see, how well the measured far-infrared wavelengths and our predictions agree.

In the case of CH_3CN we have been able to confirm unambiguously with accurate transition combination loops 15 previous assignments. In best cases our calculated wavenumbers and the experimental values agree within about 5×10^{-5} cm^{-1}. For six lines we will present a new certain assignment and for four lines there is a new idea, but seven lines are without our explanation. For CD_3CN we have unambiguously confirmed four previous assignments, in addition we have five new detailed explanations and two new tentative ideas. Two lines seem to remain without explanation.

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D18

HIGH RESOLUTION FTIR AND PHOTOACOUSTIC SPECTRA OF MONOIODOACETYLENE

Maria Saarinen, Arimatti Jutila, Peter Jungner,

Olavi Vaittinen, and Lauri Halonen

Laboratory of Physical Chemistry, P. O. Box 55 (A. I. Virtasen aukio 1),

FIN-00014 University of Helsinki, Finland

Seppo Alanko and Anne-Maaria Tolonen

Department of Physics, University of Oulu,

FIN-90570 Oulu, Finland

We have studied high resolution overtone vibration-rotation spectra of monoiodoacetylene (HCCI) in the wavenumber region 3800 - 14500 cm^{-1}. The FTIR measurements, below 10000 cm^{-1}, have been carried out with a Bruker IFS 120 HR spectrometer at a resolution of about 0.01 cm^{-1}. A multipass cell with an optical path length up to 20 meters has been used in the FTIR studies. Above 10000 cm^{-1}, a photoacoustic titanium:sapphire ring laser (Coherent 899-21) spectrometer at a resolution of about 0.02 cm^{-1} has been employed. The photoacoustic spectra show S/N > 1000 for the most intense lines of the $4v_1$ band. In contrast to the other monohalogenated acetylenes (HCCF, HCCCl, and HCCBr), only one band stemming from the ground vibrational state is observed in the $4v_1$ region.

LINE INTENSITIES IN THE FAR INFRARED SPECTRUM OF H_2O_2

A.Perrin[*], J.-M.Flaud[*], C.Camy-Peyret[*], R.Schermaul[§],
M.Winnewisser[§], J.-Y.Mandin[*], V.Dana[*], M.Badaoui[*],
J.Koput[$]

Using high resolution Fourier transform spectra ($\Re$~0.002 cm^{-1}) recorded at Giessen and at IROE, it has been possible to measure 2072 <u>relative</u> line intensities of the far-infrared spectrum of H_2O_2 in the 25-400 cm^{-1} spectral region. These intensities were introduced in a least squares fit calculation to get the expansion of the transition moment operator of the pure torsion-rotation spectrum of H_2O_2. For these intensities calculations, the theoretical model takes into account the cos γ-type dependence of the dipole moment which is due to the large amplitude torsion of the OH bonds relative to the O-O bond (2γ is the torsion angle). The value of the dipole moment obtained from the fit was then scaled to the value obtained from Stark measurements and finally a synthetic spectrum of the far infrared band of H_2O_2 was generated, using for the line intensities the dipole moment expansion determined in this work and for the line positions the parameters and the Hamiltonian matrix given in a previous analysis [C.Camy-Peyret, J.-M.Flaud, J.W.C.Johns and M.Noel, J. Mol. Spectrosc. <u>155</u>, 84-104 (1992)].

[*]Laboratoire de Physique Moléculaire et Applications, CNRS, Université Pierre et Marie Curie,Tour 13, bte 76,4 Place Jussieu, F-75252 PARIS, Cedex 05, France
[§]Physikalisch-Chemisches Institut der Justus Liebig Universitat, Heinrich Buff Ring 58, D-35392 Giessen Germany.
[$]Department of Chemistry, Adam Mickiewicz University, 60-780 Poznan, Poland.

D20

Semi-classical line-widths calculations for rovibrational lines of $^{12}CH_4$ perturbed by a rare gas

Tony GABARD

Laboratoire de Physique de l'Université de Bourgogne
U. R. A. CNRS no. 1796
6, Boulevard Gabriel, 21000 DIJON, FRANCE
EMAIL : *gabard@jupiter.u-bourgogne.fr*

Line-broadening calculations in the ν_4 band and in the ν_3 band Q branch of $^{12}CH_4$, perturbed by argon, have been performed in the framework of the semi-classical theory developed by ROBERT and BONAMY[1].

The short distance interaction potential was taken as an atom-atom LENNARD-JONES potential which parameters were fitted to existing other types of potentials (See, for exemple, Ref.[2]).

Most of the analytical calculations (derivation of the potential coefficients, calculation of resonance functions, ...) are implemented using a combination of symbolic computation and FORTRAN programs.

The energies and wavefunctions of methane used in the calculations come from analysis of interacting vibrational bands of such molecules[3].

Comparison of results with the experimental data of Ref.[4] and Ref.[5] will be shown. In particular, fine structure dependences of line-widths with respect to statistics of energy levels and typical dynamical distortions of methane will be discussed.

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D21

A TENSORIAL FORMALISM ADAPTED TO OCTAHEDRAL MOLECULES OR IONS HAVING AN ODD NUMBER OF ELECTRONS

V. BOUDON and F.MICHELOT

Laboratoire de Physique de l'Université de Bourgogne

U.R.A. C.N.R.S. n° 1796

6 bd. Gabriel, 21000 Dijon, France

A new tensorial formalism has been developed in order to handle the problem of half-integer angular momenta in octahedral symmetry. We considered the chain $SU(2) \otimes C_I \supset O_h^S$, where O_h^S is the octahedral group with its spinorial representations. The orientation of the $SU(2)$ standard $|j, m>$ basis was performed through the diagonalization of a $H^{(4,A_1)}$ operator : coupling coefficients and formulas for the computation of matrix elements were then determined[1].

We also present some applications of this formalism to the spectroscopy of hexafluorides with an odd number of electrons (like IrF_6) in a fourfold degenerate electronic state. The cases of the Jahn-Teller effect for the $\nu_2(E_g)$ and $\nu_5(F_{2g})$ modes, and of quadratic couplings for the other modes (especially the $\nu_3(F_{1u})$ mode) are considered[2].

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D22

Determination of induced dipole moments in the $v_3 = 2$ state of methane by linear Stark effect

M. Löete and M.P. Coquard

Laboratoire de Physique de L'Université de Bourgogne,
URA CNRS 1796, Faculté des Sciences,
6 Bd Gabriel, 21000 Dijon, France

H. Sasada and Y. Kuba

Department of Physics, Faculty of Science and Technology,
Keio University, 3-14-1 Hiyoshi, Kohokuku, Yokohama 223, Japan

Stark-modulation spectroscopy has been carried out for E-symmetry component of the $P(2)$ transition of the $2\nu_3$ band of methane at 1.67135 μm. Radiation generated by an external cavity semiconductor laser passed through a Stark absorption cell having a pair of electrodes spaced by 100 μm. AC Stark field of up to 30 kV_{p-p}/cm can be applied at a bias of 100 kV/cm under a sample pressure of 2.3 Torr. The magnitude of the vibrationally induced dipole moment P has been determined to be 0.0044 ± 0.0004 Debye for the $v_3 = 2$ state. The value is appreciably smaller than 0.0200 ± 0.0001 Debye for the $v_3 = 1$ state [1]. The difference between these two values is explained with our Stark Hamiltonian model[2] and the interaction between the $v_3 = 2$ and $(v_1 = 1, v_3 = 1)$ states.

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D23

A NEW SEMIRIGID BENDER MODEL FOR THE HCNO MOLECULE

THORSTEN FLÖCK AND PER JENSEN
FB 9 – Theoretische Chemie, Bergische Universität –
Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany.

In the past, the semirigid bender (SRB) model has been succesfully employed to describe the HCN bending states (involving excitation of the large amplitude HCN bending mode ν_5) superimposed on various small amplitude vibrational states of the HCNO molecule.[1,2] However, the model developed in Ref. 1 deals with small amplitude states having $v_4 = 0$ only (where ν_4 is the CNO bending mode), whereas the model of Ref. 2 describes small amplitude states with $v_4 = 1$. We present here a generalization of the semirigid bender model, with which we can describe small amplitude states with arbitrary values of v_4.

We test the new model by applying it to the $\nu_4 + v_5\nu_5$ states of HCNO, thus redoing the calculations described in Ref. 2. Further, transitions to $2\nu_4 + v_5\nu_5$ states have been experimentally observed,[3] and we hope to present a fitted HCN bending potential curve describing these states.

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D24

EXTENDED MEASUREMENTS OF THE MILLIMETER WAVE SPECTRUM OF H_2COH^+ AND ITS ISOTOPOMERS

L. Dore and **G. Cazzoli**

Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi, 2
I 40126 Bologna, Italy

S. Civiš

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the
Czech Republic, 182 23 Prague 8, Dolejškova 3, The Czech Republic

F. Scappini

Istituto di Spettroscopia Molecolare del C.N.R., via P. Gobetti, 101
I 40129 Bologna, Italy

Protonated formaldehyde was first spectroscopically identified by Amano and Warner[1] by observing the ν_1 fundamental band at 2.9 μm. Later Chomiak *et al.*[2] succeeded in observing the millimeter wave laboratory spectrum and were able to determine all the ground state quartic centrifugal distortion constants. However the D_K constant was determined by just one transition, the $11_{1,10} \leftarrow 10_{2,9}$.

In view of the astrophysical importance of the ion, we extended the lower frequency range of the rotational spectrum down to 120 GHz and measured an additional $K_a=1 \leftarrow 2$ transition in order to confirm the centrifugal distortion constant D_K[3].

In order to determine the molecular structure of this species, we are studying the rotational spectrum of the isotopomers. To date, we have assigned the spectrum of $H_2^{13}COH^+$ obtaining the rotational constants and three centrifugal distortion constants. We are presently studying the fully deuterated species.

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D25

HIGH RESOLUTION SPECTRUM OF
FLUOROCHLOROETHYNE BETWEEN 200 AND 700 cm^{-1}

Hans Bürger and M. Senzlober

Anorganische Chemie, FB 9, Universität Wuppertal,
D-42097 Wuppertal, Germany

High resolution FTIR spectra in the region of 200 to 2900 cm^{-1} of unstable fluorochloroethyne FC≡CCl were recorded between -40 and +20 °C with a Bruker 120 HR interferometer at Wuppertal employing a resolution between 2 and 5 x 10^{-3} cm^{-1}. Rotational parameters of the ground and ν_4 and ν_5 excited states have been deduced from lower state combination differences formed from cold and hot transitions in the strongly perturbed ν_1 and ν_2 bands.[1] The very weak bending fundamentals ν_4, ν_{BC} 321.27024(6) cm^{-1}, and ν_5, ν_{BC} 210.50245(5) cm^{-1} for the ^{35}Cl isotopic species, have been measured; the intensities and wavenumbers are in excellent agreement with their ab initio predictions.[1]

Rotational analyses have been performed for cold and hot bands in the ν_4 and ν_5 band regions for the two isotopic varieties. These are complemented by data from the analysis of the Σ^+ component of the $\nu_4 + \nu_5$ band, which reveals perturbations by its almost degenerate Δ component. The strong anharmonic interaction between $2\nu_4(\Sigma^+)$ and $\nu_3(\Sigma^+)$ will be discussed.

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D26

FTIR-Investigation of ^{15}N–Triazine: Ground State Constants and Rovibrational Analysis of the $\nu_{10}/2\nu_{14}$ Band System

W. Bodenmüller^{a}†, H. Essig^{a}, A. Ruoff^{a}, J. Behrend^{b},
M. Koivusaari^{c}, S. Alanko^{c}, J. Schroderus^{c}, R. Anttila^{c},
J. Walrand^{d}, and G. Blanquet^{d}

^{a} Sektion für Schwingungsspektroskopie, Universität Ulm, D–89069 Ulm, Germany.

^{b} J. Heyrovský Institute, Dolejškova 3, CZ–18223 Prague 8, Czech Republic.

^{c} Department of Physics, University of Oulu, SF-90570 Oulu, Finland.

^{d} Laboratoire de Spectroscopie Moléculaire, Facultés Universitaires N. D. de la Paix, Rue de Bruxelles, 61, B-5000 Namur, Belgium.

The isotopomer $C_3H_3^{15}N_3$ of 1,3,5–triazine (D_{3h}) has been synthesized with a isotopic purity of more than 97%. Using more than 8000 Ground State Combination Differences obtained from the analysis of the high resolution spectra of the parallel bands ν_{11} and ν_{12} and the perpendicular bands ν_7, ν_9, ν_{10}, ν_{14}, $2\nu_{14}$, and $\nu_{12} + \nu_{14}$ we were able to determine an accurate set of ground state constants.

The ν_{10} (E') fundamental is located at 663 cm^{-1} and exhibits a strong α–resonance with the overtone $2\nu_{14}^{-2}$ (E'). Furthermore the ν_{10} is connected via $l(1, 1)$-resonance to the IR-inactive parallel component $2\nu_{14}^0$ (A_1'). The essential $l(2, 2)$-resonance of both, ν_{10} and $2\nu_{14}^{\pm 2}/2\nu_{14}^0$ must be also taken into account.

More than 6000 lines of the ν_{10} (E') / $2\nu_{14}$ ($E' + A_1'$) band system have been assigned; the excited state constants and the interaction parameters will be presented at the meeting and compared with the results obtained from the analysis of the natural isotope.

D27

High resolution infrared Fourier transform spectroscopy of *Pyrrole* (C_4H_5N)

A. Held, A. Mellouki and Michel Herman
Laboratoire de Chimie Physique Moléculaire
Université Libre de Bruxelles CP 160/09 50, Av Roosevelt
1050 Bruxelles Belgium

We have used a Brucker IFS120HR to record Fourier transform absorption spectra of pyrrole between 700 and 13000 cm^{-1} with a resolution of 0.008 cm^{-1} at room temperature. We have rotationally analysed the C-H fundamental around 3150 cm^{-1}, the N-H first overtone at 6924 cm^{-1} and the fundamental out-of plane vibrational normal mode ν_{22} at 722.21 cm^{-1}. Sets of rovibrational parameters will be presented.

D28

The Anomeric Effect in Trifluoromethoxy methane, CF_3OCH_3.

Rita Kühn[a], Dines Christen[a], Hans-Georg Mack[a], Detlev Konikowski[b], Rolf Minkwitz[b] & Heinz Oberhammer[a].

[a] Institut für Physikalische & Theoretische Chemie der Universität Tübingen, 72076 Tübingen, Germany
[b] Institut für Anorganische Chemie, Universität Dortmund, 44227 Dortmund, Germany.

The molecular structure of trifluoromethoxy methane was determined by a joint analysis of gas diffraction intensities and rotational constants, incorporating a normal coordinate analysis, in order to test the predictions of the stereoelectronic effects model, the generalized anomeric effect. Due to the internal rotation of the methyl group, some lines were split and the torsional barrier, $V_3(CH_3) = 382\,(10)\,cm^{-1}$ could be determined. The rotational constants are: $B_0 = 3069.253\,(48)$ and $C_0 = 3045.581\,(48)\,MHz$. Ab initio calculations at different levels helped interpret the data.
The following structural parameters were derived (r_z-parameters in Å and deg.):
$O-C_H = 1.426\,(9)$; $O-C_F = 1.347\,(9)$; $C-F_t = 1.318\,(7)$; $C-F_g = 1.336\,(5)$; $(C-H)_{mean} = 1.095\,(24)$; $COC = 115.5\,(4)$; $(FCF)_{mean} = 107.7\,(4)$; $(HCH)_{mean} = 111.1\,(19)$; $OCF_t = 109.0\,(8)$; $OCF_g = 112.3\,(7)$.
The structure fully confirms the predictions of the anomeric effect model.

D29

Torsional Excited States in the Microwave Spectrum of Trans-2,3-Dimethyloxirane

H. Hartwig and H. Dreizler

Institut für Physikalische Chemie, Christian-Albrechts-Universität Kiel,
D-24098 Kiel, Germany

The rotational spectrum of trans-2,3-dimethyloxirane in the ground state and the fine structure due to internal rotation of the two equivalent methyl groups are well known topics [1,2]. We used our waveguide microwave Fourier transform spectrometers in the range from 8 to 26 GHz to record and assign the transitions of the first and second torsional excited states, which belong to the antisymmetric and symmetric gearing motion of the methyl tops respectivly.

To analyze the internal rotation we used an internal axis method (IAM) originaly described by Woods [3] including all top top coupling terms wich are normaly neglected. This approach leads to much faster calculation times compared to the principal axes method for two top molecules used by Meyer [4]. Comparison of both methods shows that the IAM and PAM give similar results even in the nearly degenerate torsional excited states. This will be demonstrated with calculations on propane and dimethylether.

It is also now possible to analyze some higher excited torsional states of dimethylether and dimethylether-d6 with increased accuracy compared to [5].

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D30

THE CURL-DANE-WATSON PROCEDURE WITH DAMPING FOR CALCULATING THE MOLECULAR PARAMETERS

M. Rytel and T. Rytel

Atomic and Molecular Physics Laboratory, Pedagogical University
PL-35310 RZESZÓW, Rejtana 16A, Poland

The damping in the Curl-Dane-Watson least-squares fitting of an individual band is introduced in the simple manner. The damping is a very useful tool in the nonlinear fitting thus its implementing in the Curl-Dane-Watson procedure was necessary.

The Curl-Dane-Watson fitting method[1,2] applied to the individual band gives the values of parameters and standard errors values exactly the same as in the classical proceeding. However the obtained dispersion matrix is now a block diagonal matrix. This propriety permits for subsequent independent merging of the upper and lower state parameters from different individual fits.

Authors believe that the Curl-Dane-Watson version of least-squares method should replace the classical method in the molecular spectroscopy applications.

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D31

SELF PRESSURE BROADENING IN AMMONIA:
CARS AND IR SPECTRA OF THE ν_1 BANDS
OF ^{14}NH$_3$, ^{15}NH$_3$, ^{14}ND$_3$, AND ^{15}ND$_3$

S.W. Anders, J. Jonuscheit, D. Illig, K. Sarka, M. Stamova,
and H.W. Schrötter
Sektion Physik der LMU München, Schellingstr. 4,
D-80799 München, Germany

D. Bermejo and J. Santos
Instituto de Estructura de la Materia, C.S.I.C.,
Serrano 123, E-28006 Madrid, Spain

With our cw-CARS spectrometer[1,2] we have recorded the Q-branches of the ν_1 bands of ^{14}NH$_3$, ^{15}NH$_3$, ^{14}ND$_3$, AND ^{15}ND$_3$ at pressures from 1 kPa to 80 kPa. Some preliminary results were already published[3]. For ^{14}NH$_3$ self broadening coefficients agree well with those determined from the infrared ν_1 band[4]. The CARS spectrum of ^{15}NH$_3$ was assigned by combining the wavenumbers from MW[5] and IR[6] spectra and also 24 previously unassigned IR lines could be identified. Pressure broadening coefficients had to be reduced by factors between 0.6 and 0.9 for isolated lines to obtain the best fit of experimental and simulated spectrum. In the CARS spectra of the ν_1 bands of ^{14}ND$_3$ and ^{15}ND$_3$ the lines are much more closely spaced and could not be so well resolved. To facilitate the assignment, frequency difference IR spectra[7] of these bands are being recorded in Madrid.

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D32

EFFECT OF DICKE NARROWING AND VELOCITY AVERAGING OF COLLISIONAL CROSS SECTIONS ON CO PRESSURE BROADENED LINE PROFILE.

A. Henry, M. Margottin-Maclou, D. Hurtmans, J-P. Bouanich and
A. Valentin

Laboratoire de Physique Moléculaire et Applications, C.N.R.S.
Université P. et M. Curie, 4 Place Jussieu, Tour 13 Boîte 76
F-75252 Paris CEDEX 05, France

The interference pattern obtained from a lead salt Tunable Diode Laser through a stepping Michelson interferometer allows a precise control of its emission frequency. Thus a drastic reduction of the phase noise[1] results. To suppress the effect of the variation of the intensity of the light emitted by the TDL, the ratio of the transmitted intensity over the incident intensity is measured by splitting the TDL beam in two parts. The signal to noise ratio is then of about 2000 on the transmittance.

We have studied the lineshape of three R–lines of the fundamental band of CO broadened by a foreign gas (He, Ne, N_2, Ar and Xe) at pressures ranging from 10 to 600 torr. The high resolution (a few 10^{-4} cm^{-1}) and sampling precision obtained with this system allow the accurate measurement of deviations from the Voigt profile. When the gas pressure increases from very low pressures, a narrowing of the Doppler line, as analysed by Dicke[2], occurs. This effect always holds but is progressively outdone by the shortening of the time between the phase changing collisions. This effect depends on the relative speed of the collision partners[3] and the line profile finally appears as a superposition of Lorentz profiles convolved with a modified Doppler one.

For the studied mixtures ($\approx 1\%$ of CO), the computed line profiles, accounting for Dicke narrowing and speed effects, fit the observed profiles within a few thousenths. This level of precision allows us to discuss the nature (hard or soft) of the collisions between CO and the buffer gas.

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D33

Theoretical Calculations of Pressure Broadening Coefficients
for H_2O Perturbed by Hydrogen or Helium Gas

R. R. Gamache
University of Massachusetts Lowell
Center for Atmospheric Research
450 Aiken Street
Lowell, MA, 01854 USA
and
J. B. Pollack
Space Science Division
NASA-Ames Research Center
Moffett Field, CA 94035-1000

Halfwidths were calculated for H_2O with H_2 as a broadening gas and were estimated for He as the broadening species. The calculations used the model of Robert and Bonamy with parabolic trajectories and all relevant terms in the interaction potential. The calculations investigated the dependence of the halfwidth on the order of the atom-atom expansion, the rotational states, and the temperature in the range 200 to 400K. Finally, calculations were performed for many transitions of interest in the 5 μm window region of the spectrum. The resulting data will be used for extracting accurate water mixing ratios from the analysis of the thermal channels for the Net Flux experiment on the Galileo probe.

D34

LINE COUPLING IN ANISOTROPIC RAMAN Q BRANCHES : APPLICATION TO THE $\nu_1/2\nu_2$ FERMI DYAD OF CO_2

L.Bonamy

Laboratoire de Physique Moléculaire, U.R.A. C.N.R.S. 772
Université de Franche-Comté
25030 Besançon Cedex, France

B.Lavorel, G.Fanjoux, and G.Millot

Laboratoire de Physique de l'Université de Bourgogne
U.R.A. C.N.R.S. 1796
6 bld Gabriel, 21000 Dijon, France

The Energy Corrected Sudden (ECS) model is based on the infinite-order-sudden (IOS) approximation under which the rotational angular momentum J does not relax. Here, the ECS model is generalized to enforce the relaxation of J and of its associated higher-order tensors. Then, the spectroscopic cross sections are calculated by taking into account the angular momentum coupling between vibration, rotation and radiation. This description is used to calculate the Q branches of the anisotropic Coherent anti-Stokes Raman Scattering (CARS) spectra corresponding to the the ν_1 and $2\nu_2$ transitions of the Fermi dyad of CO_2. This model permits to evidence drastic decouplings from isotropic to anisotropic lines.

The corresponding experimental spectra have been recorded with the polarized CARS technique for pressures leading to a consistent overlapping between the rotational components. It is shown that the observed dip in the ν_1 Q branch is due to a residual contribution of the isotropic part of the spectrum which is already known from a previous study. This leads to a new experimental evaluation of the relaxation time of the second order tensor J^2 associated with the rotational angular momentum J. The value is in excellent agreement with that already obtain from the study of the infrared absorption Q branch, the Rayleigh scattering and the viscomagnetic effect.

D35

THE ELECTRIC DIPOLE MOMENT OF AMMONIA DIMER FOR G:|K|=1
(band origin 747.2 GHz)

GINA COTTI[§], HAROLD LINNARTZ[†] and W. LEO MEERTS[‡]

[§] *Dip. chimico "G. Ciamician", Universita' degli studi di Bologna via Selmi 2, 40126 Bologna, Italy*

[†] *Inst. für Angewandte Physik, Wegelstrasse 8, D53115 Bonn, Germany*

[‡] *Dept. of Molecular and Laser Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

In the last years it was generally accepted that the so called 'ammonia dimer riddle' is a pure consequence of the dynamical character of this complex. Recent Stark measurements on the G:|K|=1 (band origin at 486 GHz) [1] also provided *structural* information. In this contribution additional results on another G:|K|=1 state will be presented.

From the results of Stark measurements performed in a molecular jet expansion the electric dipole moment of both the ground and the excited state are determined. The measurements were performed with the Nijmegen tunable far infrared spectrometer [2] and the Stark set up is the same as described in Ref.[1] : two metal plates (15x5.4x1 cm) are positioned on both sides of the nozzle, parallel to the slit of the nozzle, 5 cm apart.

We observed the Stark pattern for the two R(1) and for the two Q(1) transitions with an electric field of about 40 V/cm and since the far infrared radiation is polarized both parallel and perpendicular to the electric field, both $\Delta M=0$ and $\Delta M=\pm 1$ were observed.

Preliminary results give a dipole moment value of 0.76(2) D for the ground state and 0.37(1) D for the excited state and theoretical predicted values [3] are in good agreement with them.

We therefore confirm the conclusion of the former electric dipole moment determinations that the ammonia dimer reflects an averaged antiparallel structure.

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D36

SEMIEMPIRICAL MODEL OF THE COOPERATIVITY EFFECT IN THE CONJUGATED HYDROGEN-BOND BRIDGES A–H...B

G. V. Yukhnevich

Institute of General and Inorganic Chemistry,

Russian Academy of Sciences,

Leninsky prosp. 31, Moscow 117907, Russia

The concept of the nature of the cooperativity effect is developed in the frame of the Elyashevich-Wilson theory of molecular vibrations. Protonodonor and protonoacceptor abilities of any A–H group is believed to vary linearly under the influence of the same properties of other A–H groups connected with the considered one via a sequence of hydrogen bonds. Unknown coefficients in these correlations can be determined from the independent spectroscopic data[1]. These coefficients being estimated enable one to calculate all dynamical and electrooptical parameters of conjugated and non-conjugated bridges A–H...B composing the system under consideration. The set of parameters found thus far makes it possible in principle to calculate the whole vibrational spectrum of the hydrogen-bonded molecular system of any chemical composition and structure.

Present status of experimental data enables one to find necessary parameters and to calculate vibrational spectra of systems composed from such species as H_2O, CH_3OH or HF. An application of this model to $(HF)_n$ clusters gave quite natural explanation of the spectra taken with the use of size-selection technique[2] which met some contradictions with theroretical estimates[3].

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D37

Multi-Nozzle jet Fourier Transform Spectroscopy

R. Georges, M. Bach and M. Herman

Laboratoire de Chimie Physique Moléculaire CP160/09
Université libre de Bruxelles
Roosevelt ave., 50
B-150, Belgium

We have build a multi-nozzle jet system in front of a Bruker IFS120HR Fourier Transform Interferometer*. The set-up will be described. Results allowing to discuss various characteristics of the system (detection sensitivity, rotational and vibrational cooling, geometry of the multi-jets), will be emphasised, in particular with v_3, N_2O. Experimental evidence for the presence of large N_2O clusters will be presented.

* R. Georges, G. Durry. M. Bach, R. Pétrisse, R. Jost and M. Herman, submitted for publication (Chem. Phys. Letters).

D38

RETRIEVAL OF VERTICAL CONCENTRATION PROFILES OF STRATOSPHERIC CONSTITUENTS FROM BALLOON-BORNE FOURIER TRANSFORM SPECTROSCOPY

S. Payan[1], C. Camy-Peyret[2], P.Jeseck[2], T. Hawat[3] and G. Durry[2]

(1) Comissariat à l'Energie Atomique (CEA), Centre d'Etudes Scientifiques et Techniques d'Aquitaine (CESTA), BP n°2, 33114 Le Barp, France

(2) Laboratoire de Physique Moléculaire et Applications (LPMA) CNRS/UPMC , tour 13, Bte 76, 4 place Jussieu, 75252 Paris cedex 05, France

(3) Institut d'Electronique et de Micro-Electronique du Nord (IEMN) O.A.E., CNRS/UMR 9929, 59304 Valenciennes, France

High resolution infrared spectroscopy from balloon is a powerful technique to retrieve the vertical profiles of atmospheric constituents with high sensitivity and good vertical resolution. The LPMA (Limb Profile Monitor of the Atmosphere) Fourier transform infrared spectrometer is a remote-sensing instrument operating under stratospheric balloons and designed to perform trace species measurements in absorption using the sun as source.

Two successful flights, respectively in october 1994 from Aire-sur-l'Adour (France) and in march 1995 from Kiruna (Sweden), have been conducted during SESAME (Second European Stratospheric Arctic and Mid-latitude Experiment). The technique developed for the analysis of the spectra will be discussed and the first results will be presented. To calculate a synthetic spectrum, the atmosphere is divided into a number of thin (1 km) homogeneous layers (spherical shells) and the overall atmospheric transmission is computed (including refraction effects) from the transmission of each layer for all the spectra recorded for various solar elevation (or depression) angles during ascent and sunset (at float). A model atmosphere combined with local meteorological soundings and best a priori estimates for molecular composition are used. Within each layer effective temperature and pressure are taken as air mass weighted averages along the line of sight. The spectroscopic line parameters are extracted from the HITRAN 92 database. A global fit is applied to all the selected micro-windows containing information on one or several species. It is possible to vary the parameters of the instrumental function together with the local background and a possible wavenumber shift. The retrieved concentration profiles result from a nonlinear least-squares program (based on the standard Levenberg-Marquardt algorithm) which minimizes the differences between the observed and synthetic spectra. The method has been used for the retrieval of the vertical mixing ratio profiles of HCl, NO_2 and CH_4 in the 3.3 μm region. A discussion of performances in term of precision, stability and computer resources is presented.

D39

NOVEL METHODS FOR QUANTITATIVE GAS ANALYSIS AT MILLIMETRIC WAVELENGTHS

N D Rezgui, J G Baker, and J Allen
Department of Physics and Astronomy
Univesity of Manchester, M13 9PL, UK
J F Alder
Department of Instumentation and Analytical Science
UMIST, P.O Box 88, Manchester M60 1QD, UK

A frequency modulated Fabry-Perot cavity spectrometer with piezoelectric tuning[1] has been operated at frequencies from 70 GHz to 183 GHz to detect samples present in air down to 380 ppb concentration. We have exploited its capability of maintaining the cavity at resonance by carrying out scans in which the sample pressure is varied continuously between 1 Pa and several kPa whilst the absorption.is monitored. In addition to the expected signal peak in the 5-10 Pa region, we have observed a rising absorption pedestal extending to very much larger pressures for a number of absorbers including OCS, SO_2,H_2CO, and CH_2CHCN. We interpret this pedestal as arising from the overlap of numerous adjacent absorption lines, and propose its use in extending mmwave spectral analysis to atmospheric pressure samples.

We also report the use of frequency scans at lower pressures in which the dispersive rather than the absorptive component of a spectral line is displayed by monitoring the piezoelectrically controlled cavity mirror spacing, and show that this technique is also capable of good sample sensitivity whilst dispensing with the need for a high performance millimetre wave detector.

1 N D Rezgui, J G Baker, J Allen, and J F Alder, Anal. Chim. Acta. (1995), in press.

D40

INFORMATION SYSTEM AIRSENTRY
FOR MODELING RADIATIVE TRANSFER IN THE ATMOSPHERE,
BASED ON HIGH-RESOLUTION MOLECULAR SPECTRA

V.F.Golovko, A.V.Nikitin, A.A.Chursin

LTS, Institute of Atmospheric Optics, 1, Akademicheskii Av., Tomsk

634055, Russia

and

Vl.G.Tyuterev

GSMA, Faculté des Sciences, Université de Reims, REIMS Cedex, France

The application AIRSENTRY (Atmospheric Infra-Red Spectra for Emulating and Noting the Transmission of RaYs) is a MS Windows version of our previous program GRASSP. At present, the last Turbo-Pascal version GEISA-PC of this kind of software is developed in collaboration with the ARA group at Laboratoire de Météorologie Dynamique (LMD, France).[1] Commonly, a line-by-line method is used to calculate the absorption contour from line parameters.

AirSentry program contains a number of new features that allow us to compute the radiative transfer in the atmosphere in a single scattering approximation, continuous absorption of water, refraction index and to process the absorption spectra measured.

Capabilities to edit the standard random access files and the files in the text mode, such as: databanks of line parameters, atmospheric constituent and temperature profiles, partition functions, aerosol models, a list of species, and so on make this code attractively flexible for users.

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D41

TEMPERATURE DEPENDENT UV-VIS CROSS SECTIONS OF NO$_2$ AND O$_3$ FOR THE GLOBAL OZONE MONITORING EXPERIMENT ONBOARD THE ENVIRONMENTAL RESEARCH SATELLITE - 2

A. Dehn, B. Deters, S. Himmelmann, A. Türk, M. Weißenmayer, and J.P. Burrows

Institute of Environmental Physics, University of Bremen
P.O. Box 330440, D-28359 Bremen, Germany
e-mail : dehn@gome3.physik.uni-bremen.de

We present details about the calibration of the Global Ozone Monitoring Experiment on board the ERS-2 Satellite, which was carried out before its launch on April 21, 1995. Temperature dependent reference spectra of ozone and NO$_2$ were recorded. GOME measures from 240 nm to 790 nm, where the whole range is covered by four channels with an overlap of about 10 nm respectively.

The calibration was done using the CATGAS instrument (Calibration Apparatus for Trace Gas Spectra), which was designed at University of Bremen. It consists of a double jacketed quartz cell including a White optic. One jacket is filled by a cooling fluid (here ethanol). Data were taken at temperatures from 202 K up to 293 K. The inner jacket was flushed by the different atmospheric gases. A combination of either a tungsten or a deuterium lamp was used together with a diode array.

The so received relative spectra had to be converted into absolute cross sections. The amount of NO$_2$ is determined from the emission rate of a permeation-tube. In the case of ozone, we obtained the cross sections by titration of ozone with NO.

D42

ROTATION - TORSION EFFECTIVE HAMILTONIAN
FOR DINITROGEN PENTOXIDE

M.Kreglewski

Adam Mickiewicz University, 60-780 Poznan, Poland

The ab initio calculation [1] and the electron diffraction study [2] indicate that the dinitrogen pentoxide, N_2O_5, has a non-planar structure. The plane of the molecule is defined by the bent N-O-N skeleton. Two nitro groups , NO_2, are twisted out of this plane by ±30 degrees.

The potential determined in an electron diffraction study [2] has been used for the calculation of the torsional levels and their splittings due to the tunneling. The conclusion is that the tunneling splittings should not perturb the ground state rotational spectrum of N_2O_5. In the first excited torsional state the splittings should be at least 300 kHz. The splittings can not be observed directly in the spectrum due to the nuclear spin statistics of ^{16}O atoms which removes half of the rotational levels. However, the splittings shift the other half of the rotational levels. In order to fit the rotational spectrum in the excited torsional state of N_2O_5 one should add to an effective rotational hamiltonian terms originating from the torsional tunneling.

Following this result a phenomenological group-theoretical hamiltonian, based on the model of slow tunneling, is proposed. The hamiltonian has been derived using the G_{16} permutation - inversion molecular symmetry group of N_2O_5. The different paths of the torsional tunneling are identified.

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D43

RETRIEVAL OF SPECTRAL LINE PARAMETERS IN PA-SPECTROSCOPY OF DERIVATIVE WITH THE TWO-FREQUENCY LASER

V.A.Kapitanov, M.Yu.Kataev and O.Yu.Nikiforova

Institute of Atmospheric Optics,

1, Akademicheskii Ave., 634055, Tomsk, Russia

The experimental data obtained with two-channel PA-spectrometer (Photo-Acoustic) with a dye laser are presented in this report. The characteristic features of the experiment were the follows:

- the PA-detectors were placed inside the laser cavity;

- the laser operated in two-frequency mode of lasing;

- the measured parameters were the frequency-derivative of spectrum.

In order to retrieve the spectral line parameters (e.g., line halfwidth and shift), the experimental data were processed using two methods, namely, the least-squares method and the direct search method. The initial values of spectral line parameters were chosen using the method of direct search. Then the parameters were detailed using the least-squares method.

Broadening and shift coefficients were obtained from measurement data on contours of H_2O lines broadened by acetone and air.

E1

Rotational spectroscopy of B⋯XY in pre-reactive mixtures of Lewis bases B and halogens or interhalogens XY

A.C. Legon

Department of Chemistry, University of Exeter
Stocker Road, Exeter EX4 4QD, United Kingdom

Pulsed-nozzle, Fourier-transform microwave spectroscopy has been used to investigate the nature of the intermolecular binding in a series of complexes B⋯XY, where B is a Lewis base and XY is a halogen or interhalogen. For several of the simpler, more interesting Lewis bases, mixing of B and XY leads to a chemical reaction. In some cases, *e.g.* acetylene and chlorine, the reaction can be vigorous and hence the components cannot be pre-mixed. To avoid reactions of this type, a fast-mixing nozzle has been employed. The reactive components remain separate in this device until the point at which they expand coaxially into the vacuum chamber of the spectrometer. Any complexes formed in this mixing process achieve collisionless expansion within approx. 10 μs or so and are effectively frozen. They can then be rotationally polarized using pulses of microwave radiation and the subsequent free induction decay recorded in the usual way.

Several features of the ground-state rotational spectra of B⋯XY so observed are revealing of the nature of the interaction. The form of the spectra and the magnitudes of the rotational constants allow conclusions about the angular geometry. The Cl-nuclear quadrupole coupling constants $\chi_{aa}(Cl_x)$ (x = i for inner, o for outer) associated with the two Cl nuclei in B⋯Cl$_2$, for example, can be interpreted to give a measure δ of the extent of electron redistribution from Cl$_i$ to Cl$_o$ on formation of the complex. The centrifugal distortion constants D_J (linear or symmetric-top molecule) or Δ_J (asymmetric-top molecule) are inversely proportional to the intermolecular stretching force constant k_σ in the quadratic approximation and assuming rigid subunits and thereby provide information about the strength of the interaction.

Systematic variation of B and XY indicates how the determined properties (angular geometry, δ and k_σ) vary along series B⋯XY and allows some general conclusions about the nature of the B⋯XY interaction.

E2

SINGLE MOLECULE SPECTROSCOPY IN LOW-TEMPERATURE SOLIDS : A REVIEW

B. Lounis, Ph. Tamarat, R. Brown and M. Orrit,
C. P. M. O. H., C.N.R.S. et Université Bordeaux I, 351 Cours de la
Libération, 33405 Talence Cedex, France

The fluorescence excitation spectra of small and dilute samples of solid solutions kept at helium temperatures display the sharp homogeneous lines of individual solute molecules[1,2]. Since their first observation in 1990, these lines have been the subject of much work, which will be reviewed in the lecture. In addition to the general appearance of single molecule lines (width, intensity, distribution), their behavior under external perturbations such as electric fields or pressure was investigated. The different shifts point to differences in the microscopic environment.

Very soon, the time-dependence of the fluorescence signal was recognized and put to use to characterize dynamics within the molecule (intersystem crossing, Rabi precession, emission) as well as in the surrounding matrix (spectral diffusion of the resonance frequency). The auto-correlation method enables one to study processes with characteristic times ranging from nanoseconds to minutes.

During the last two years, new experiments were performed on single molecules. First, single pentacene molecules in p-terphenyl crystals demonstrate paramagnetic resonance in their triplet states. Microwave pulses were used to produce transient effects, or to trigger the pulse with the observed photon itself. Emission spectra of single molecules are a signature of their chemical nature and are affected by molecular environment. Non-linear optical experiments of the pump-probe type can be done on the narrow excitation lines, and show light-shift and Autler-Townes-like splittings. Finally, images of individual molecules have been obtained optically by different methods, opening exciting possibilities of combining spectral with spatial resolutions[3].

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F1

AN AB INITIO CALCULATION OF THE ROVIBRONIC ENERGIES OF THE CH_2^+ MOLECULE

PER JENSEN AND M. BRUMM

FB 9 – Theoretische Chemie, Bergische Universität –
Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany.

W. P. KRAEMER

Max-Planck-Institut für Astrophysik, Karl-Schwarzschild-Strasse 1,
Postfach 1523, D-85740 Garching, Germany.

P. R. BUNKER

Steacie Institute for Molecular Sciences, National Research Council of
Canada, Ottawa, Ontario, Canada K1A 0R6.

In a recent paper[1] we reported the results of an *ab initio* calculation of the vibronic (i.e., $N = 0$) energy levels of the CH_2^+ molecular ion in both the $\widetilde{X}\ ^2A_1$ and $\widetilde{A}\ ^2B_1$ electronic states. These two electronic states become degenerate ($^2\Pi$) when the molecule is linear, and in the vibronic calculation we used the theory that we have given in another paper[2] in order to allow for the effects of the electronic angular momentum in this situation (i.e., the Renner effect). In the present work we extend the CH_2^+ calculation to include $N > 0$ rovibronic energies and we take into account the effect of spin-orbit coupling by using the *ab initio* value of the spin-orbit matrix element from Reuter and Peyerimhoff[3]. The only experimental data available for CH_2^+ come from a measurement of the ν_3 fundamental band of the ground state[4] in which the ν_3 vibrational term value was determined to be 3131.37 cm^{-1}. In our *ab initio* calculation we obtain 3114.1 cm^{-1} for this term value. Thus, to make our predictions as reliable as possible, we calculate the rovibronic energies after adjusting one parameter in the potential so that we fit the observed value of the ν_3 vibrational term value. Using this slightly adjusted *ab initio* potential we predict a large number of rovibronic term values in the $\widetilde{X}$ and $\widetilde{A}$ states that have not yet been spectroscopically characterized, and we compare our results for the line positions and spin splittings in the ν_3 band with the observations.

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F2

OBSERVATION OF HIGH J VALUES IN THE v'=2,3,4 AND 5 VIBRATIONAL LEVELS OF THE PHOTODISSOCIATION SPECTRUM OF THE b←a SYSTEM OF O_2^+.

M. Larzillière, C. Frigon, C. J. Délisle and N. Varfalvy

Laboratoire de physique atomique et moléculaire

Département de physique, Université Laval

Québec Canada G1K 7P4.

P.C. Cosby

Molecular Physics Laboratory, SRI International

Menlo Park, CA, 94025.

The laser-ion beams coaxial geometry, characteristic of the fast ion beam-laser spectroscopy (FIBLAS) method, allows a detailed study of transitions into predissociated levels of the O_2^+ $b^4\Sigma_g^-$ state with sub-Doppler optical resolution. A radio-frequency ion source is found to populate very high rotational levels (J $\leq$ 50.5) in O_2^+, allowing a significant extension in the range of rotational levels heretofore observed in the b a system. Over 400 new absorption lines, distributed over (v',v") = (2,2), (3,3), (4,4) and (5,5) vibrational bands have been mesured by FIBLAS. A determination of precise molecular constants for the a and b states also requires the accurate measurements of transitions involving lower rotational levels in these states. This is achieved by measurement of the b→a emission spectrum using a Fourier Transform spectrometer. Eight emission bands, (0,0)-(0,3), (1,0) and (1,3)-(1,5), are analysed and combined with the FIBLAS bands and previous photofragment measurements to obtain a consistent set of molecular constants describing the O_2^+ $b^4\Sigma_g^-$ and $a^4\Pi_u$ states.

F3

The $D^2\Sigma^+$ -$X^2\Sigma^+$ Transition of the CaBr and CaI Radicals

Elena CASERO-JUNQUERA, Djemila BENHABIB, Joëlle ROSTAS and Guy TAIEB

Laboratoire de Photophysique Moléculaire du CNRS
Institut de Physico-Chimie Moléculaire de l'Université de Paris-Sud
Bat. 213, Université de Paris-Sud, 91405 ORSAY Cedex, France

Laser excitation spectra have been recorded for $Ca^{79}Br$, $Ca^{81}Br$ and CaI in the 310-330 nm spectral region.

The radicals are produced in a Broida oven through the reaction: $Ca(^1S)$ + R-X —> CaX + R, where X=Br, I, and R=$CHBr_2$, C_3H_7. They are rotationally relaxed (T=350K) by a fast Helium flow. The laser frequency of a YAG pumped dye laser is doubled through a KDP crystal.

The vibrational structure of the CaBr and CaI shows striking contrast. As expected for a $D^2\Sigma^+$-$X^2\Sigma^+$ transition of a CaX compound, the CaBr spectrum consists of a series of single-headed bands degraded to the violet. The presence of two Br isotopes of approximately equal abundance causes the spectrum to be highly congested and overlapped. The most prominent peaks have been assigned to the v_D-0_X (v_D = 0-2) progression, and (0-1) band. Molecular constants for the $D^2\Sigma^+$ state of CaBr derived from the vibrational and rotational band envelope analysis of the observed spectrum will be presented.

The CaI spectrum presents: i) on the red side, two groups of four peaks, separated by about $\omega_e(X)$, and ii) on the blue side, two more sets of bands of different structures, and not obviously related in position with the red part of the spectrum. Further experiments have been carried out: i) two-photon resonance enhanced excitation via the A and B states, resulting in a series of narrow peaks, which have been tentatively assigned as part of the D-X transition[1]; ii) OODR excitation in the (31090±6) cm⁻¹ region via the $A^2\Pi_{3/2}$ component, resulting in 20 single rotational lines. Further rotationally resolved spectra of pertinent regions of the spectrum are still needed in order to fully understand the structure of the D state of CaI.

The electrostatic ligand-field model developped by R.W. Field and coll.[2] , which successfully describes the (X, A, B) ionic states of the alkaline-earth compounds, seems inadequate for the D state of CaI. This may indicate that covalent states play a major role in the D state energy range. Extensive *ab initio* calculations would greatly help in the characterization of the electronic states around and above 3.7 eV, which are involved in the 310-330 nm region of the CaI spectrum.

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F4

HIGH RESOLUTION SPECTROSCOPIC ANALYSIS OF $E0_g^+ \rightarrow A1_u(^3\Pi_u)$ AND $E0_g^+ \rightarrow B''1_u(^1\Pi_u)$ TRANSITIONS IN THE I_2 MOLECULE

R. Bacis, D. Cerny, S. Churassy, D. Inard, M. Nota, A.J. Ross and V.Skorokhodov*

Université Lyon I, Laboratoire de Spectrométrie Ionique et Moléculaire, URA171 - 43, Bd. du 11 Novembre 1918, 69622 Villeurbanne Cedex.
*Institute of Physics, St. Petersbourg State University, ul. Ulyanovskaya 1, Petrodvorets, St. Petersbourg, 198904, Russia.

The $E0_g^+ \rightarrow A1_u(^3\Pi_u)$ and $E0_g^+ \rightarrow B''1_u(^1\Pi_u)$ fluorescence has been recorded at high resolution (.150 cm^{-1}) in the range 28600-31600 cm^{-1}, using the direct optical-optical double resonance : $E0_g^+ \leftarrow B0_u^+ \leftarrow X0_g^+$. The two-photon excitation was performed with two single-mode ring dye lasers in order to excite only one single rovibrational level of the $E0_g^+$ state. All spectra show a strong collisional transfer from $E0_g^+$ to $D0_u^+$ with a prominent $\Delta J = \mp 1$ rule. Both 1_u states correlate with the ground-state I atoms.

Only the lower part of $A1_u$ potential was previously characterized experimentally. In this work, it has been possible to extend the analysis until v"= 34. The main spectroscopic constants are, in cm^{-1}: $T_e = 10905,6$ (1), $\omega_e= 92,9$ (3), $\omega_e x_e = 1,5$ (2) and $B_c= 0,0275$ (3). The well depth has been calculated to be $D_e = 1640$ cm^{-1} and $v_D \simeq 50$.

The experimental data for $B''1_u$ state were previously extremely scarse. The potential curve is essentially unbound (in the region $r < 3$Å) and only the repulsive branch was known [1,2]. The bound part of the potential ($r_e \simeq 4$Å) has been extrapolated by Tellinghuisen [3]. In our work, we characterized almost the whole well depth, from v"=0 to 20 (estimated $v_D \simeq 24$). With about 780 observed lines the following values had been derived, in cm^{-1} : T_e=12344,9 (1), $\omega_e= 19,9$ (4), $\omega_o x_c = 0,498$ (2), $B_e = 0,01455$ (3) and D_e=202 (2) cm^{-1}.

Ω-doubling variation with v" was analysed and long range behaviour characterized for both electronic states.

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F5

SPECTROSCOPY OF CrCl: OBSERVATION AND ANALYSIS OF THREE BAND SYSTEMS IN THE NEAR INFRARED

R.Koivisto and O.Launila

Department of Physics, Stockholm University
Box 6730 S-11385 Stockholm, Sweden

Fourier transform spectra of the CrCl radical have been recorded in emission at a temperature of 1100°C, using a ceramic furnace a source. The spectral region 6900-11700 cm^{-1} was covered with a resolution of 0.025 cm^{-1}. A preliminary analysis of the bands indicates that the (0,0) sequences of the $A^6\Sigma^+-X^6\Sigma^+$ and $B^6\Pi-X^6\Sigma^+$ transitions of CrCl are located at 9460 and 8870 cm^{-1}, respectively. A third electronic system is also present in the spectrum. This weaker system appears to have no counterpart in the corresponding CrF spectrum, and we suggest that the system might be due to a quartet transition.

The $A^6\Sigma^+$ state suffers from local perturbations. The causes of these perturbations are not clear at present, although it seems likely that at least one of the $B^6\Pi(v=2)$ spin components is perturbing the $A^6\Sigma^+(v=0)$ level.

The appearance of the bands is extremely complex, although they are fully resolved. The analysis is based on interactive analyzing techniques, particularly *Loomis-Wood* methods and iterative use of synthesizing, fitting and spectral manipulation routines. These routines permit an almost fully computerized rotational analysis to be made in many situations where the huge number of rotational lines along with the associated bookkeeping problems would be a major limiting factor for the whole project.

F6

The ν_2, ν_6, and ν_7 Fundamentals of NC-CC-CN

F. Winther, Abt. Chem. Physik,

Institut für Physikalische Chemie,

D-24098 Kiel, Germany

Dicyanoacetylene (C_4N_2) has nine fundamentals of which five are Raman-active, only. This means that precise ro-vibrational constants must be determined from difference bands in high resolution infrared spectra.

Results concerning the bands ν_2- ν_9, ν_6- ν_9, ν_6+ ν_8- ν_6, ν_4- ν_7, and ν_7+ν_8-ν_7 shall be presented. From these the following energy levels have been deduced:

ν_2= 1 (Σ_g^+) = 2123.070 cm^{-1}

ν_6 = 1 (Π_g) = 504.663 cm^{-1}

ν_7 = 1 (Π_g) = 261.054 cm^{-1}

F7

LASERSPECTROSCOPY OF THE B ← X TRANSITION OF KAr

H. Valipour and D. Zimmermann
Institut für Strahlungs- und Kernpyhsik
Technische Universität Berlin
Hardenbergstr. 36, D-10623 Berlin

The absorption spectrum of the van der Waals molecule KAr has been observed by means of high-resolution laserspectroscopy for wavenumbers between 13055 and 13080 cm^{-1} using a tunable laser diode as a light source ($\lambda \approx$ ˙65 nm). About 420 absorption lines due to the transition $B^2\Sigma \leftarrow X^2\Sigma$ have successfully been assigned to the rotational structure of 8 vibrational bands with $v' = v_0, \ldots v_0+3$ and $v'' = 0, 1$. Up to now, the value of v_0 could not be determined, but we expect v_0 to be 1 or 2 from theoretical considerations. Our direct observation of rovibrational levels of the $B^2\Sigma$ state represents a major step towards a complete understanding of the system of the two nearby electronic states $A^2\Pi$ and $B^2\Sigma$ which for KAr are strongly coupled by the non-diagonal part of the spin-orbit-operator. The rovibrational levels of the $A^2\Pi$ state have been studied previously in detail /1/ providing, however, only indirect information on the $B^2\Sigma$ state.

/1/ F. Bokelmann and D. Zimmermann: Laserspectroscopy of the $A^2\Pi \leftarrow X^2\Sigma$ transition of KAr, to be published

F8

SPIN-ORBIT INTERACTIONS BETWEEN $c^3\Sigma^+$ AND $B^1\Pi$ STATES OF ScF AND ScCl: EFFECTS ON THE FINE AND HYPERFINE STRUCTURES

M.-A. Lebeault-Dorget[1], F. Taher[1], C. Effantin[1], A. Bernard[2],
J. d' Incan[1], E. A. Shenyavskaya[3], and J. Vergès[4]

[1] *Laboratoire de Spectrométrie Ionique et Moléculaire, Université Claude Bernard, Lyon I, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France* [2] *Observatoire de Lyon, 69561 Saint-Genis-Laval, France* [3] *Thermocentre of the Russian Academy of Sciences, Institute for High Temperatures, Izorskaya 13/19 Moscow 127412, Russia* [4] *Laboratoire Aimé Cotton, CNRS II, 91405 Orsay, France*

Anomalies in the fine and hyperfine structures of the close-lying $c^3\Sigma^+$ and $B^1\Pi$ states of ScF and ScCl are explained in terms of spin-orbit interactions between them.

For ScF, the $c^3\Sigma^+, B^1\Pi \rightarrow X^1\Sigma^+$ transitions both appear. Vibrational levels of equal v of the two interacting states are close together with corresponding overlap integrals between wavefunctions nearly unity. These global $v \sim v$ interactions have consequences on both states e. g., anomalously large effective values of the Λ-doubling and spin-splitting parameters, and changes in the hyperfine structures of the f levels, correlated to the degree of mixing (maximum at $v=0$).

For ScCl, very localized perturbations affect $B^1\Pi(v=0$ to $4)$ levels, of the type $c^3\Sigma^+(v+2) \sim B^1\Pi(v)$, and on account of the smallness of corresponding overlap integrals, significant changes in the hyperfine structures of the f levels are only seen in the neighborhood of the maximum of the perturbations. $c^3\Sigma^+ \rightarrow X^1\Sigma^+$ transitions do not appear (except for a few extralines).

Deperturbed molecular constants are obtained. The vibration-indepedent spin-orbit interaction parameters are found, $\xi_{el}=56.4$ cm^{-1} for ScF, and about 65 cm^{-1} for ScCl, close to the Sc$^+$ two-electron atomic value, $\zeta=^2/_5 |E_{Jmax}-E_{Jmin}|\approx 71$ cm^{-1}, in the 3d4s (^{3}D) state.

Hyperfine structure is attributed to strong interaction between the s electron of the $4s\sigma 3d\sigma$ configuration and the Sc nucleus of spin 7/2. Modeling of observed line profiles gives the value $b_F=0.032\pm0.008$ cm^{-1} of the Fermi contact term in $c^3\Sigma^+$ (ScF).

F9

High Resolution Electron Impact Study of the Emission Spectrum of Molecular Hydrogen

Xianming Liu, Syed M. Ahmed, Geoffrey K. James, Joseph M. Ajello
Jet Propulsion Laboratory, California Institute of Technology
4800 Oak Grove Drive, Pasadena, CA 91109, U.S.A.

Donald E. Shemansky, Hong-Yao Hu
Aerospace Engineering Department, University of Southern California
Los Angles, CA 90089, U.S.A.

Hervé Abgrall, Evelyne Roueff
Observatoire de Paris, Section de Meudon, DAEC and CNRS URA 173
92195 Meudon Cedex, France

Françoise Launay
Observatoire de Paris, Section de Meudon, DAMAP and CNRS URA 812
92195 Meudon Cedex, France

Jean-Yves Roncin
Laboratoire Traitement du Signal et Instrumentation, CNRS URA 842
23 rue Dr. P. Michelon, 42023 Saint-Etienne Cedex 2, France

The emission spectrum of molecular hydrogen produced by electron impact excitation at 100 eV, and the excitation function of the Lyman and Werner band systems have been measured. Optically thin high resolution spectra ($\Delta \lambda = 0.136$Å) in the wavelength range from 1140 to 1690 Å and optically thin medium resolution spectra ($\Delta \lambda = 0.90$Å) from 900 to 1200 Å have been obtained. Synthetic spectral intensities based on the transition probabilities calculated by Abgrall *et al* and the newly measured excitation functions are in very good agreement with experimentally observed intensities. Previous modeling utilizing Allison-Dalgarno band transition probabilities with Hönl-London factors breaks down when the transition moment has significant J dependence or when ro-vibronic coupling is significant. Ro-vibronic perturbation between v=14 of the B $^1\Sigma_u^+$ state and v=3 of the C $^1\Pi_u$ state and the rotational dependence of the transition moment in (6,12) and (7,13) bands of the Lyman system are examined. Experimental excitation cross-sections of the Lyman and Werner systems and high resolution reference spectra, together with the model synthetic spectra based on the transition probabilities calculated by Abgrall *et al*, will be presented. An improved spectrometer calibration standard is obtained.

F10

EFFECTIVE OPERATORS APPROACH FOR GLOBAL TREATMENT OF VIBRATIONAL-ROTATIONAL SPECTRA OF NITROUS OXIDE

V.I.Perevalov ,O.M.Lyulin
Institute of Atmosferic Optics, Russian Academy of Sciences,
Siberian Branch, Akademicheskii av., 634055 Tomsk, Russia

J.-L. Teffo
Laboratoire de Physique Moléculaire et Applications, C.N.R.S.,
Université Pierre et Marie Curie, Boite 76, 4 Place Jussieu, 75252
Paris-cedex 05, France

The effective operators method has been applied to the global treatment of vibrational-rotational spectra of nitrous oxide. For this purpose a reduced effective Hamiltonian which contains resonance interaction terms due to the approximate relations between harmonic frequensies $\omega_3 \approx 2\omega_1 \approx 4\omega_2$ has been suggested. The experimental values of spectroscopic constants G_v, B_v, and D_v, mostly those of Toth[1], have been fitted to the parameters of this Hamiltonian. Using the eigenfunctions of this effective Hamiltonian two kinds of fittings of experimental intensities of Toth[2] to the parameters of an effective dipole moment operator have been performed. In the first of them the rotationless electric-dipole transition moments have been fitted whereas in the second one line intensities have been fitted. The regions of $2\nu_2$, $3\nu_2$, $4\nu_2$, $5\nu_2$ and $6\nu_2$ bands have been investigated. To check the extrapolational properties of both effective Hamiltonian and effective dipole moment operator we have predicted the band intensities of some forbidden bands ($\Delta\ell_2 = 2$). The predicted and experimental values of band intensities of forbidden bands are in a good agreement.

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F11

Laser optogalvanic Study of HCO ($\tilde{A}^2A$" - $\tilde{X}^2A'$) Using a Ti:Sapphire Laser

J.L. Destombes, I. Hadj Bachir, T. Huet, A. Zellagui

Laboratoire de Spectroscopie Hertzienne, associé au C.N.R.S.
Université des Sciences et de Technologie de Lille
59655 villeneuve d'Ascq Cedex, France

The (050)-(000) band of the HCO $\tilde{A}^2A$" - $\tilde{X}^2A'$ transition is recorded using a Titanium Sapphire laser spectrometer. The HCO radical is produced in a radio frequency discharge in acetaldehyde (CH_3CHO) vapor mixed with argon/helium. The $\tilde{A}$ - $\tilde{X}$ transition in the (13130-13240 cm^{-1}) region is detected by laser induced changes in the discharge impedance. Rotational transitions have been measured with higher resolving power than in an earlier work [1] and with an absolute accuracy of 0.007 cm^{-1}. The analysis of rotational lines shows a broadening greater than the Doppler width (≈ 0.3 cm^{-1}). This phenomenon may be interpreted by the interaction of the $\tilde{A}$ state with nearby strongly predissociated levels as already discussed for the (090)-(000) band by Vasudev and Zare [2]. Experimental energy data have been fitted by fixing ground state parameters [3] and by varying those of the upper state [1], this has allowed to calculate rotational constants of the $\tilde{A}$ state with a best precision.

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F12

BIFURCATION IN ROTATIONAL SPECTRA
OF NONLINEAR AB$_2$ MOLECULES

I. N. KOZIN

Applied Physics Institute, Russian Academy of Science,
Uljanov Street 46, 603600 Nizhnii Novgorod, Russia.

AND

I. M. PAVLICHENKOV

Russian National Center "Kurchatov Institute",
123182 Moscow, Russia.

A classical microscopic theory of rovibrational motion at high angular momenta in symmetrical non-linear molecules AB$_2$ is derived within the framework of small oscillations near the stationary states of a rotating molecule. The full-dimensional analysis including stretching vibrations has confirmed the existence of the bifurcation predicted previously by means of the rigid-bender model[1]. The formation of four-fold energy clusters resulting from the bifurcation has been experimentally verified for H$_2$Se [2] and it has been demonstrated in fully-dimensional quantum mechanical calculations carried out with the MORBID computer program[3].

We show in the present work that apart from the level clustering, the bifurcation produces physically important effects including molecular symmetry-breaking and a transition from the normal mode to the local mode limit for the stretching vibrations due to rovibrational interaction. The application of the present theory with realistic molecular potentials to the H$_2$Te, H$_2$Se and H$_2$S hydrides results in predictions of the bifurcation points very close to those calculated previously. However for the lighter H$_2$O molecule we find that the bifurcation occurs at higher values of the total angular momentum than obtained in previous estimations. The present work shows it to be very unlikely that the bifurcation in H$_2$O will lead to clustering of energy levels. This result is in agreement with recent variational calculations.

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F13

MILLIMETER-WAVE AND INFRARED SPECTROSCOPY OF BrC^{15}N : EQUILIBRIUM STRUCTURE OF CYANOGEN BROMIDE.

F. Tamassia, C. Degli Esposti, L. Dore, and G. Cazzoli

Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna.
Via F. Selmi 2, 40126 Bologna - Italia

The rotational spectra of ^{79}Br^{12}C^{15}N and ^{81}Br^{12}C^{15}N in the low-lying $01^{1}0$, $10^{0}0$, $02^{0}0$ and $02^{2}0$ vibrational states have been observed in the millimeter-wave region, and the ν_3 fundamental band (C-N stretch) has been recorded from 2125 to 2195 cm^{-1} with a computer controlled diode laser spectrometer in a triple beam configuration. A very precise equilibrium structure has been calculated for cyanogen bromide combining the obtained data with those already known for the normal isotopomers:

$$r_e(\text{C-Br}) = 1.78750 \pm 0.00004 \text{ Å}$$
$$r_e(\text{C-N}) = 1.15951 \pm 0.00005 \text{ Å}$$

The newly determined C-N distance agrees now much better with those of the similar ClCN and ICN molecules.

The ground state rotational spectra of ^{79}Br^{13}C^{15}N and ^{81}Br^{13}C^{15}N have been also observed, so that r_0, r_s, and r_m structures could be evaluated from the ground state moments of inertia of eight different isotopic species. The results agree well with the theoretical expectations, that is a progressively better approximation of the r_e structure is obtained passing from the r_0 to the r_s and r_m geometries.

F14

H$_2$S SPECTRUM FROM 0.9 TO 5 µm: THE POLYADE STRUCTURE and SPECTROSCOPIC PARAMETERS

L.R. Brown, J. Crisp, and D. Crisp
Jet Propulsion Laboratory, California Institute
of Technology, Pasadena, CA 91109, USA
A.Bykov, O.Naumenko, M.Smirnov, and L.Sinitsa
Institute of Atmospheric Optics, Tomsk,
634055, Russia
A.Perrin
Laboratoire de Physique Moléculaire et Applications,
CNRS, Université Pierre et Marie Curie,
Tour 13, bte 76,4 Place Jussieu,
F-75252 PARIS, Cedex 05, France

The absorption spectra of H$_2$S from 0.8 to 5 µm have been recorded with spectral resolutions of 0.006, 0.012 and 0.021 cm^{-1} using the Fourier transform spectrometer at Kitt Peak National Observatory. The line centers were determined with the accuracy varying from 0.0004 cm^{-1} for strong, isolated lines to 0.001 cm^{-1} for weak or blended lines. The intensity measurements were also carried out with the average accuracy of ±5 % for isolated lines. The transitions of 20 bands have been assigned for the first time so that accurate energy levels, band origins and vibrational parameters have been determined (1). This paper is devoted to the analysis of the rotational structure of the recorded H$_2$S bands. The energy levels of the second triad, first and second hexade and first decade of resonating states of H$_2^{32}$S , H$_2^{34}$S and H$_2^{33}$S molecule will be presented together with Watson-type Hamiltonian parameters. The analysis of H$_2$S highly excited states revealed some interesting features in the energy spectrum, e.g. fourfold clustering of rotational levels belonging to the symmetric and asymmetric components of local mode manifolds at a high degree of stretching excitation. Analysis of the intensities allowed us to determine the transformed dipole moment parameters for all polyades allowing the extensive and accurate line intensity calculations. The research described in this publication was made in part by grants No.NY3000 and No.NY3300 from the International Science Foundation.

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F15

NIR SPECTRAL BANDS OF ACETYLENE MEASURED BY HIGH RESOLUTION DIODE LASER SPECTROSCOPY:
$\nu_1 + 3\nu_3$ and $\nu_1+2\nu_2+\nu_3+4\nu_4^0$ revisited

J G Baker, D Li* and N J Bowring
Department of Physics and Astronomy
University of Manchester, M13 9PL,UK

Measurements on the acetylene nir absorption spectrum have been made been made between 783 and 790 nm using an improved home built scanning laser diode spectrometer with a frequency precision of 0.003 cm^{-1} and a sensitivity of the order of 10^{-27} mols.atm.$^{-1}$ cm.$^{-2}$. Frequencies have been checked both by the use of ground state combination relations and by interlacing acetylene and water calibration spectra. Observed spectral line strengths range over four orders of magnitudeand, and we have sought out forbidden transitions in an attempt fully to explain the complex resonant structures reported for the bands in this region by ourselves and other workers.[1,2]

Best fits and comparisons between predicted and experimental spectral patterns for both $\nu_1 + 3\nu_3$ and $\nu_1+2\nu_2+\nu_3+4\nu_4^0$ bands are presented, with a view to identifying the precise combination of Fermi, Coriolis and l-type resonances responsible for the structures observed.

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* Present address: Harvard School of Medicine, Boston, Mass, USA

F 16

ASSIGNMENT AND PRELIMINARY ANALYSIS OF THE IR ABSORPTION SPECTRUM OF CH$_3$D IN THE REGION 1900-3200 CM^{-1}

Nikitin A.[1], Champion J.P.[2], Tyuterev Vl.G.[3] and Brown L.R.[4]

(1) Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 634055 Tomsk, Russia.
(2) Laboratoire de Physique URA CNRS 1796, Université de Bourgogne, 6 Boulevard Gabriel, 21000 Dijon, France.
(3) GSMA, URA CNRS D 1434, Faculté des Sciences, BP 347, 51062 Reims, France.
(4) Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109 USA.

The infrared spectra of CH$_3$D in the region 1900-3200 cm^{-1} has been investigated using high-resolution Fourier spectra recorded at Kitt Peak. This region includes the nine interacting vibrational bands: $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_4(E)$, $2\nu_3(A_1)$, $2\nu_5(A_1+E)$, $2\nu_6(A_1+E)$, $\nu_3+\nu_5(E)$, $\nu_3+\nu_6(E)$ and $\nu_5+\nu_6(A_1+A_2+E)$.

Starting from assignments available in HITRAN, the analysis process could be initiated leading on turn to an extented assignment of the new spectra involving all vibrational bands. However in the present stage, due to problems encountered with two of the bands, the fit was limited to small values of J.

The investigation of such a complex polyad (so-called Nonad) required to develop an appropriate model based on the tensorial formalism allowing a coherent description of the successive polyads of the molecule. The Hamiltonian was expressed as a sum of terms relating directly to the subsequent Polyads: Ground State, Triad and Nonad. Doing so, the effects of the rovibrational interactions taking place in the Triad system (1) are consistently extrapolated into the Nonad system. Theoretical details including relationships between our parameters and classical parametres are described elsewhere (2).

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F17

A DETAILED ANALYSIS OF THE $\nu_2/\nu_5/\nu_3 + \nu_6$
BAND SYSTEM OF $^{13}CH_3I$ and $^{12}CH_3I$

Seppo Alanko

Department of Physical Sciences, University of Oulu

Linnanmaa, 90570 Oulu, Finland

In the literature a great number of publications concerning the compli-
cated band system $\nu_2/\nu_5/\nu_3+\nu_6$ of $^{12}CH_3I$ can be found, see for example
Ref.[1] and references therein. However, no full analysis with complete
energy matrices and with all the interactions taken simultaneously into
account, seems to be available. So, as we are now in process of analysing
the $\nu_2/\nu_5/\nu_3 + \nu_6$ band system of $^{13}CH_3I$, we decided to analyse it for
$^{12}CH_3I$, too.

In both the isotopomers the resonance picture is rather similar. In addi-
tion to the main interactors $\nu_2(A_1)$, $\nu_5(E)$, and $\nu_3 + \nu_6(E)$ two overtone
levels $2\nu_3(A_1)$ and $3\nu_3(A_1)$ were added to the model to check certain fea-
tures in the spectra. So, our model consists of two degenerate and three
non-degenerate vibrational levels. In the calculations a computer pro-
gram developed by F. Hegelund et al.[2] originally for D_{2d} molecule allene,
was applied. The program was first changed to meet the requirements
of C_{3v} molecules and finally adapted to this problem, in particularly.
For a given value of the quantum number J the complete Hamiltonian
matrix is first set up and then symmetry factorised into A_1, A_2, and
E blocks. The dimensions of these matrices are about $(\frac{7}{3})J,(\frac{7}{3})J$ and
$(\frac{14}{3})J$, respectively. In the program the highest calculated K value is
25 $(K'_{max} = 17$ in the spectrum) and so the dimension of the E block
matrix with J higher than 25 $(J_{max} \approx 90)$ never exceeds 120.
The details of the analysing methods and the results for the analyzed
bands will be presented.

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F18

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF STIBINE
IN THE GROUND, $v_2 = 1$, AND $v_4 = 1$ VIBRATIONAL STATES.
EXTENSION OF THE EFFECTIVE HYPERFINE HAMILTONIAN

H. Harder and C. Gerke
Institut für Physikalische Chemie der Universität Kiel,
Olshausenstr. 40-60 D-24098 KIEL, Deutschland

L. Fusina and G. Di Lonardo
Dipartimento di Chimica Fisica e Inorganica, Università di Bologna,
Viale Risorgimento 4, I-40136 BOLOGNA, Italia

Using the technique of waveguide Fourier transform microwave spectroscopy in the 1 to 12 GHz range, we observed $\Delta J = 0$, $A_1 - A_2$ splitting transitions for both $^{121}SbH_3$ and $^{123}SbH_3$, with $kl = +1$, -2, and +4 in the $v_4 = 1$ state and with $k = 3$ in the ground and $v_2 = 1$ states. Furthermore, we were able to detect $\Delta k = 3$ "forbidden" transitions in the $v_2 = 1$ state. The transitions showed hyperfine patterns whose components were measured with an accuracy ranging from 0.3 to 300 kHz.

In a previous investigation, $kl = +1$, $A_1 - A_2$ transitions and $J = 18$, $kl = +12$ pure quadrupole transitions in the $v_4 = 1$ state were observed and analysed [1]. The theory of quadrupole rotation-vibration interactions developed by Aliev and Hougen [2] was applied for the first time. The extremely precise data obtained in this work noticeably extend the J and K range of observation and can be used to test the theoretical model.

All the available data were used simultaneously to provide precise values of the spectroscopic parameters. In order to reproduce the observed transitions with an accuracy comparable to the experimental one, the theory for quadrupole coupling [2], and the equivalent for spin-rotation coupling [3], have been extended to higher order terms. In addition, it was necessary to include in the model the spin-vibration term [4]. The analysis led to precise values of both diagonal and off-diagonal quadrupole and spin-rotation parameters. Some of these have been determined for the first time.

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F 19

TUNABLE FAR INFRARED SPECTROSCOPY OF H_2O_2

G. Di Lonardo, L. Fusina and E. Venuti

Dipartimento di Chimica Fisica e Inorganica, Università di Bologna,

Viale Risorgimento 4, I-40136 BOLOGNA, Italia

M. Bellini, E. Catacchini, P. De Natale and M. Inguscio

European Laboratory of Nonlinear Spectroscopy (LENS), Department of

Physics, Università di Firenze, Largo E. Fermi 2, I-50125 FIRENZE, Italia

The far-infrared spectrum of H_2O_2 has been recorded by means of a tunable FIR spectrometer operating at LENS, Firenze. About 40 transitions have been measured in the 2.8 - 3.4 THz spectral region, with gas pressure in the 5 - 33 Pa range. They belong to the $^rQ_4$ and $^rQ_5$ sub-branches, which are the most prominent features in the upper atmosphere emission spectrum of this molecule, of the transition between the lowest torsional states The analysis of the data has been made on the basis of a theoretical model which includes the interaction between the $(n,\tau) = (0,1)$ and $(1,1)$ states.

Stark measurements have also been performed on three selected transitions, namely the $2_{2,0} - 1_{1,0}$ at 1272297 MHz, the $8_{2,6} - 7_{1,6}$ at 882451 MHz and the $9_{2,8} - 8_{1,8}$ at 962933 MHz. Accurate values of the dipole moment of the molecule have been obtained by taking into account the interaction between the levels involved in the transitions and nearby near resonant levels.

F20

Analysis of the rotation-vibration in the
$v_2 = 1$, $v_3 = 1$, $v_5 = 1$ and $v_6 = 1$ states of CDF_3

J. Cosléou, J. Demaison, M. Khelkhal, H. Fichou
Laboratoire de Spectroscopie Hertzienne, URA CNRS 249,
Bât P5, Université de Lille 1,
59655 VILLENEUVE D'ASCQ France

M. Paplewski, H. Bürger,
Anorganische Chemie, FB 9, Universität-Gesamthochschule,
D 42037 WUPPERTAL, Germany

C. Gerke and H. Harder
Institut für Physikalische Chemie, Abteilung Chemische Physik,
Universität Kiel, Olshausenstrasse 40-60,
D 24098 KIEL Germany

The infrared spectra of the v_2, v_3, v_5 and v_6 fundamental bands of CDF_3 have been recorded with a high resolution (0.003 cm^{-1}) FTIR spectrometer (BRUKER IFS 120HR).

The K structure of the $v_2=1$ and $v_3=1$ states was clearly resolved and the assignment was straightforward. Measurements from a previous analysis of millimeter-wave spectra were added[1]. Rotational constants and quartic and sextic centrifugal distorsion parameters have been determined accurately.

Direct ℓ-type resonance transitions in the $v_5=1$ and $v_6=1$ states were observed between 2 and 24 GHz and splittings of the $|k-l| = 3$ transitions were measured. Such splittings were also observed in the $v_5=1$ state in the submillimeter, FTIR and high resolution sidebands CO_2 laser spectra.

For these two excited states, two different sets of parameters were used to fit the data because the effective Hamiltonian may be reduced in different ways. The unitary equivalence of both sets of parameters is verified.

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F21

SEMINUMERICAL CONTACT TRANSFORMATION: FROM INTERNAL COORDINATE ROVIBRATIONAL HAMILTONIAN TO EFFECTIVE ROTATIONAL HAMILTONIANS. FRAMEWORK OF THE METHOD.

Tuomas J. Lukka and Esa Kauppi

Laboratory of Physical Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1),

FIN-00014 University of Helsinki, Finland

A formulation of seminumerical contact transformations usable in rovibrational spectroscopy is presented. Effective rotational Hamiltonians are obtained starting from a rovibrational Hamiltonian with an exact kinetic energy operator in curvilinear internal valence coordinates. Like the accuracy of the variational methods, the accuracy of this method can be increased by using more computational power. Error estimates are also calculated. Main motivations for using seminumerical contact transformations are considered. As an example, a calculation is carried out for H_2S. No remarkable deviations between the calculated and observed effective constants were observed for the states considered. New ideas for further research of this subject are suggested.

F22

NEW TREATMENT OF A TWO OSCILLATOR SYSTEM. APPLICATION TO MOLECULAR DOUBLY DEGENERATE VIBRATIONAL MODES

V. BOUJUT and F. MICHELOT

Laboratoire de Physique de l'Université de Bourgogne,

U. R. A C.N.R.S. . n° 1796

6 bd Gabriel, 21000 Dijon, France

Based on Schwinger's realization of su(2), a new method is proposed for the treatment of a two interacting oscillator system. Elementary creation and annihilation operators. b_i^+ and b_i (i = 1, 2) are associated with tensors of half-integer rank. The construction of arbitrary operators as well as state labeling are then performed in the whole algebraic chain, named "standard ", u(2) $\supset$ su(2) $\supset$ so(2).

This procedure has two interesting consequences : 1) general expressions for the matrix elements of operators of arbitrary degree are obtained. 2) the results of the standard basis are straightforwardly adapted to vibational mode with an "E" symmetry type whatever the point symmetry group G.

F23

SOME NEW ASPECTS IN THE LOCAL MODE AND NEAR LOCAL MODE APPROACHES IN MOLECULES

O.N.Ulenikov

Laboratory of Molecular Spectroscopy, Physics Department, Tomsk State University, Tomsk, 634050, RUSSIA

R.N.Tolchenov

Laboratory of Spectroscopy, Siberian Institute of Physics, Tomsk, 634050, RUSSIA

Local mode method was modified on the base of carefull analysis of transformation coefficients $l_{N\alpha\lambda}$ and properties of intramolecular potential function. Method was applied to XY_2, XY_3, ZXY_3, XY_4, X_2Y_2 molecules. It was shown that even in the framework of strict local mode approach known in literature relations between some spectroscopic parameters should be modified. New relations between centrifugal distortion coefficients and some other fourth spectroscopic parameters were obtained. It was shown that the knowledge of centrifugal parameters of gro- und vibrational states of above mentioned molecules gives possibility to predict both the band centers and rovibrational energy spectra of deformational bands even in con- ditions of total absence of any information about these deformational bands.

F24

MICROWAVE SPECTRA AND STRUCTURE OF CF$_2$=NH AND CF$_2$=NCl

Peter Groner and James R. Durig
Department of Chemistry, University of Missouri - Kansas City,
Kansas City, MO, U.S.A.
Daryl D. DesMarteau,
Department of Chemistry, Clemson University, Clemson, SC, U.S.A.

The microwave spectra of ^{13}CF$_2$^{14}NH, ^{12}CF$_2$^{15}NH and ^{12}CF$_2$^{15}ND were recorded and analyzed. The resulting rotational constants are (in MHz):

^{13}CF$_2$^{14}NH: A = 11465.015(11), B = 11147.348(11), C = 5642.240(11);

^{12}CF$_2$^{15}NH: A = 11453.869(4), B = 10706.849(4), C = 5524.437(4);

^{12}CF$_2$^{15}ND: A = 11379.147(3), B = 9947.971(3), C = 5299.006(3).

The dipole moment of ^{12}CF$_2$^{15}NH ($|\mu_a|$ = 0.24(1) D, $|\mu_b|$ = 1.42(1) D) is evidence of rotation of the principal axes system by about 8° with respect to the principal axes system in ^{12}CF$_2$^{14}NH.

The rotational lines and their complex quadrupole hyperfine structure in the microwave spectra of ^{12}CF$_2$^{15}N^{35}Cl, ^{12}CF$_2$^{15}N^{37}Cl, and ^{13}CF$_2$^{14}N^{35}Cl were analyzed. The resulting rotational constants are:

^{12}CF$_2$^{15}N^{35}Cl: A = 11091.673(2), B = 2541.6909(3), C = 2066.2883(2);

^{12}CF$_2$^{15}N^{37}Cl: A = 11091.652(2), B = 2470.6085(4), C = 2019.0565(4);

^{13}CF$_2$^{14}N^{35}Cl: A = 11260.951(2), B = 2534.5910(7), C = 2067.3693(6).

The quadrupole coupling constants of Cl obtained from a global least squares fit of all assigned hyperfine components are (in MHz):

^{12}CF$_2$^{15}N^{35}Cl: χ_{bb} - χ_{cc} = -26.07(2), χ_{aa} = -71.33(5), χ_{ab} = 64.5(2);

^{12}CF$_2$^{15}N^{37}Cl: χ_{bb} - χ_{cc} = -20.50(4), χ_{aa} = -56.2(3), χ_{ab} = 51.1(10);

^{13}CF$_2$^{14}N^{35}Cl: χ_{bb} - χ_{cc} = -25.84(3), χ_{aa} = -71.38(9), χ_{ab} = 62.8(11).

The analysis for ^{13}CF$_2$^{14}N^{35}Cl required the exact diagonalization of the complete rotational-hyperfine Hamiltonian because, in some cases, the (first order) quadrupole splittings of the ^{14}N and ^{35}Cl nuclei were accidentally of the same size. Reanalysis of the data of ^{12}CF$_2$^{14}N^{35}Cl and ^{12}CF$_2$^{14}N^{37}Cl resulted in χ_{ab} of 62.8(13) and 50.5(16) MHz for these species, respectively, more than 20% larger than in the original analysis [1].

The new results were used together with the data on the normal isotopic species of CF$_2$NH [2,3] and CF$_2$NCl [1,4] to derive the molecular structures.

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F25

ROTATIONAL AND ROVIBRATIONAL SPECTRA OF
CHClF$_2$ IN ALL STATES WITH POPULATION
FACTORS>·4% AND OF ITS ^{13}C ISOTOPOMER

S.Blanco[a], G.Cazzoli[b], J.M.Colmont[a], G.Cotti[b],
G.Graner[c], Z. Kisiel[d], I.Merke[c], and L.Pszczółkowski[d]

[a]LSH, Université de Lille I, 59655 Villeneuve d'Ascq, France
[b]Department of Chemistry, Universita' di Bologna, 40126-Bologna, Italy
[c]LPMA, CNRS, Université de Paris-Sud, 91405-Orsay, France
[d]Institute of Physics PAN, Al.Lotnikόw, 02-668 Warszawa, Poland

Results of a concerted effort to analyse the rotational and rovi-
brational spectrum of the atmospherically important molecule CHClF$_2$
(HCFC-22) are presented. As a consequence of the concern about the
ozone layer this substance is currently in use as one of the major replace-
ments for the previous generation of refrigerants and its environmental
monitoring has increased in importance. This work was carried out
within the research network SCAMP of the European Union[a] with the
aim of providing benchmark spectroscopic data for accurate monitoring
of this substance in the atmosphere and for refining *ab initio* calculations.

The spectrum of the ground state and of the two lowest lying excited
states, ν_9 and ν_6 of parent isotopic species have recently been studied
by some of the present authors. Those data are presently complemented
by accurate results on all remaining vibrational states that have room
temperature, natural abundance population factors higher than 4%. We
report the analysis of high-resolution spectra in the ground state and in
the two lowest excited states, ν_9 and ν_6 of the CH^{37}ClF$_2$ species, and
in the ν_5 state of the CH^{35}ClF$_2$ species. In addition the spectrum of
the ^{13}CH^{35}ClF$_2$ has been observed and analysed for the first time. In
all cases complete sets of sextic level spectroscopic constants have been
determined from the analysis of rotational and vibration-rotation spectra
recorded on a variety of high resolution spectrometers and frequencies
from 10 GHz through to 450 cm^{-1}. The Coriolis interaction between
$v_9 = 1$ and $v_6 = 1$ states of CH^{37}ClF$_2$ is also analysed in terms of
coupling about both c and a inertial axes and the results are compared
with those for the parent species.

F26

ANALYSIS OF THE ν_3 BAND OF ND_2H

L. Francou, **F. Rachet**, **A. Valentin**, and **L. H. Coudert**,

Laboratoire de Physique Moléculaire et Applications
Unité Propre du C.N.R.S., Université Pierre et Marie Curie
Tour 13 - Case Courrier 76 - 4 Place Jussieu
F-75252 Paris Cedex 05, France

The ground vibrational state as well as the ν_2 band of the two partially deuterated species of ammonia, NH_2D and ND_2H, have been studied a few years ago using either microwave,[1] far-infrared,[2] or infrared[3-4] spectroscopy. The other vibrational bands of these species, however, have received little attention.

In the present paper, an investigation of the ν_3 band of ND_2H will be reported. For the two symmetrical species NH_3 and ND_3, the upper vibrational state of this band is an E-type doubly-degenerate state. However, for the unsymmetrical ND_2H species, this degeneracy is lifted because of the lack of three-fold axis of symmetry, and the ν_3 band actually consists of two bands about 200 cm^{-1} apart. Starting from the infrared spectrum of ND_2H, recorded with a Fourier transform spectrometer in the 2400–3100 cm^{-1} region, an analysis of the upper band has been undertaken. Several hundred transitions have been assigned and a preliminary analysis of their wavenumbers have been carried out using the same approach as previous investigators[1] to account for the inversion doubling.

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HIGH RESOLUTION FTIR SPECTRUM OF THIOCARBONYLDIFLUORID SCF_2

Hans Bürger and Wolfgang Jerzembeck

Anorganische Chemie, FB 9, Universität Wuppertal,
D-42097 Wuppertal, Germany

Unstable SCF_2 has been prepared by thermolysis of the cyclic dimer. Its IR spectrum has been recorded using the Bruker 120 HR interferometer at Wuppertal operating at a resolution of ca. 0.003 cm^{-1}. The spectral region $330 - 1410$ cm^{-1} was investigated and all fundamentals $\nu_1 - \nu_6$ and the two combination bands $\nu_2 + \nu_3$ and $\nu_2 + \nu_5$ have been studied.

SCF_2 is a planar asymmetric rotor ($\kappa = -0.6264$) with C_{2v} symmetry. The six fundamental vibrations and their symmetry properties are: $3A_1$ (ν_1, ν_2 and ν_3), $2B_1$ (ν_4 and ν_5) and $1B_2$ (ν_6). These give rise to pure A, B and C type bands, respectively. Rovibrational analyses were performed of the unperturbed bands ν_2 (ν_0 $785.535187(18)$ cm^{-1}), ν_5 (ν_0 $419.545800(13)$ cm^{-1}) and ν_6 ($623.187297(12)$ cm^{-1}). Rovibrational parameters up to quartic terms have been determined using Watsons Hamiltonian in A reduction and I^r representation, typically 5000 transitions being fitted for each band with a standard deviation of 3×10^{-4} cm^{-1}.

F28

MICROWAVE SPECTRUM OF *SYN* OXALYL FLUORIDE[1]

K.-M. Marstokk and Harald Møllendal

Department of Chemistry, University of Oslo, P. O. Box 1033 Blindern

N-0315 Oslo, Norway

The microwave spectrum of oxalyl fluoride has been investigated in the 10.0 - 39.0 GHz spectral region at dry-ice temperature (–78 °C). The *syn* confomer having the two carbonyl groups and the two C-F bonds *syn* to each other was assigned. This rotamer has a *planar* equilibrium conformation.

Nine excited states of the torsion were assigned. The torsional fundamental frequency was determined to be $26(5)$ cm^{-1}. The rotational constants of the ground and of six excited states were used to determine the shape near the bottom of the potential well of the *syn* conformer in terms of a dimensionless parameter z as $V(z) = 7.0 (<z^4> + 2.0 <z^2>)$ cm^{-1}. The *full* potential function has also been approximated by $V(\phi) = \Sigma (\frac{1}{2} V_n (1 - \cos(n\phi))$ and the three first constants determined to be $V_1 = 2.24$, $V_2 = 9.59$, and $V_3 = 0.26$ kJ mol^{-1}. The transition state lies $10.9(20)$ kJ mol^{-1} above the *anti* minimum for $\phi = 90(3)^\circ$. Absolute intensity measurements have been used to determine the Gibbs free energy difference at 195 K between *syn* and *anti* as $\Delta G^0 = 1.7(5)$ kJ mol^{-1} (*anti* more stable than *syn*.) The entropy difference, $\Delta S^0 = 5.1(1)$ J K^{-1} mol^{-1}, was found using statistical mechanics. The enthalpy difference is $\Delta H^0 = H_{syn} - H_{anti} = 2.7(6)$ kJ mol^{-1}. The dipole moment of *syn*-oxalyl fluoride is $3.652(83) \times 10^{-30}$ C m.

The microwave work was assisted by *ab initio* computations. At the MP2/6-311+G* levels of theory, the *anti* conformer is computed to be 2.2 kJ mol^{-1} more stable than *syn* with a transition state lying 7.6 kJ mol^{-1} above the energy of the more stable *anti* conformer. This in good agreement with the experimental findings.

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F29

Five-membered cyclic Ketones: The Rotational Spectra of isotopic substituted Cyclopentenones

R. Ruoff, A. Krebs, T. Schaeffler, G. Stiegler
and
H.-K. Bodenseh
Universität Ulm, Abteilung Chemische Physik
Albert-Einstein-Allee 11
D-89069 Ulm

In connection with the investigations of the structure of Cyclopentadienone[1] we used the experiences in preparing isotopic substituted cyclopentenones to measure their microwave spectra, too.

To obtain more detailed information as described by Chadwick et al.[2] we assigned a greater number of rotational transitions in the ground vibrational state and the first exited vibrational state of the ring bending mode. In two syntheses we prepared 3-deuterocyclopentenone and a mixture of 4- and 5-deuterocyclopentenone and assigned their ground state spectra. For the 3d-isotopomer the first two excited states of the ring bending mode could also be assigned.

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F30

FREE JET ABSORPTION MILLIMETERWAVE SPECTRUM OF THIOANISOLE.

B. Velino
Dipartimento di Chimica Fisica e Inorganica Viale Risorgimento 4, 40136
Bologna Italy.

S. Melandri

Istituto di Spettroscopia Molecolare del C.N.R.,via Gobetti 101,40129
Bologna Italy.

W. Caminati and P. G. Favero

Dipartimento di Chimica "G. Ciamician" Via Selmi 2,40126 Bologna
Italy.

The microwave spectrum of thioanisole has been assigned using a free jet
millimeter wave spectrometer in the frequency range 60-78 Ghz.

The carbon atom of the methyl group was found to lie in the benzene
ring plane.

The potential energy functions hindering the CH_3X (X=O,S) rotation
are proposed for thioanisole and anisole.

F31

The microwave spectrum of ABCO-H$_2$O and DABCO-H$_2$O determined by Molecular Beam Fourier Transform Microwave Spectroscopy

D. Consalvo

Institut für Physikalische Chemie, Christian-Albrechts-Universität Kiel,

D-24098 Kiel, Germany

W. Stahl

Institut für Physikalische Chemie, RWTH Aachen,

D-52056 Aachen, Germany

Several investigations on van der Waals and hydrogen bonded complexes have been undertaken using a pulsed molecular beam Fourier transform spectrometer (MB-FTMW) at Kiel. Yet, not many microwave studies on hydrogen bonded complexes have been reported in literature where the monomer is an amine. 1-Azabicyclo[2.2.2]octane (ABCO) and 1,4-Diazabicyclo[2.2.2]octane (DABCO) are both tertiary amines. Their protonation in water produces the corresponding cathions and HO⁻ anions.

From the observation of symmetric top spectra of the water complexes, it has been deduced that water undergoes internal rotation. In case of ABCO-water the N...H-O bond length and its harmonic stretching force constant available from centrifugal distortion constants have been determined.

The hyperfine pattern due to the ^{14}N nuclear quadrupole moment has been resolved. Using a reasonable model for the interaction potential, it has been possible to estimate the torsional barrier of water.

F32

Application of evolution strategies
in nonlinear least-squares fit procedures for spectroscopic data

Y. Heiner[*], J. Waschull[*], B. Sumpf[**], H.-D. Kronfeldt

Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1
Str. des 17. Juni 135, D-10623 Berlin, Germany
e-mail: yvonne@marie.physik.tu-berlin.de

Up to now the method of Levenberg and Marquardt is the standard algorithm for nonlinear least-squares curve-fitting[1] not restricted to the field of spectroscopy. But is this well established method the most suitable procedure for spectroscopic applications?

In recent years some efforts have been made to use evolutionary algorithms, i.e. to apply the principles of the biological evolution to curve fitting. Whereas the procedures developed base on genetic algorithms we present fits using an evolution strategy applied to high resolution spectra of polyatomic molecules in the mid-infrared region.

The results are compared to such obtained with the Levenberg-Marquardt method under the same initial conditions. Three cases of synthesized and real spectra will be discussed: single lines (H_2S), groups of three lines (NO_2) and crowded spectra (C_6H_6). We demonstrate in which cases we found the application of evolution strategies preferable over the conventional method.

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F33

LINE BROADENING AND SHIFT IN THE ν_3 $^{12}CO_2$ AND $^{13}CO_2$ BANDS

S. Marchetti R. Simili

IFAM-CNR ,Via del Giardino 7 , 56100 Pisa , Italy

A pulsed , LN_2 cooled, tunable diode laser (Laser Analytics), operating in the 4.4 μm region ,has been used to measure the pressure broadening and pressure shift of the ν_3 high J number (> 50) CO_2 lines in fundamental transition and some related (lower J) isotopic and hot bands . The theory [1] foresees about a 4.5MHz/mb self-broadening ,but larger values (5-13MHz/mb) are measured. Equivalent measurements are observed on the 30<J<70 lines of several hot bands.

Much larger broadening has been observed in the low J lines for the isotopic $^{13}CO_2$ transitions ,ranging from 8 to 40MHz/mb ,with the larger values measured for the direct 0->1 band . Inside this vibrational band the larger values are observed for the more populated J levels (14-22) showing a kind of a strong rotational resonance[2]. In addition a large blue shift (1-6 MHz /mb)is also observed for this isotopic 0->1 band .This surprising blue shift is confirmed by the N_2 broadening and shifting in the same band. In fact the observed N_2 broadening coefficients are in the 3-5 MHz/mb range , (quite in agreement with the theory) but a J dependent blue shift in the 0.1-1 MHz/mb range is surprisingly observed .

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F34

Pressure broadening in the v_{14} band of benzene

J.Waschull[*], Y.Heiner[*], B.Sumpf[**], H.-D. Kronfeldt
Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1
Straße des 17. Juni 135, 10623 Berlin, Germany
e-mail: yvonne@marie.physik.tu-berlin.de

A pulse driven diode laser spectrometer was applied to measure high resolution spectra of benzene between 1014 cm^{-1} and 1053 cm^{-1}.

The high line density of the benzene spectrum requires measurements at comparatively low gas pressures (up to 3 Torr) which became possible using a Herriott multipass cell (optical pathlength about 5 m). For data treatment we used a line fit procedure based on an evolution strategy. The details of which are given in a separate poster by Y. Heiner et al.

We are able to present quantum number dependencies of the self- and air-broadening coefficients. Additionally we investigated the nobel gas broadening (He, Ne, Ar, Kr, Xe) of some Q-branch lines.

F35

Analysis of the branch shapes in CO_2 15 μm spectrum.

N. N. Filippov and <u>M. V. Tonkov</u>
Institute of Physics, St.Petersburg University,
Peterhof, 198904 St.Petersburg, Russia

A new approach for the theoretical analysis of infrared band shapes is proposed. The computational method based on the well-known infinite order sudden approximation (IOSA),[1] is developed for linear molecules. The cross-section for coupling between lines $j_i \rightarrow j_f$ and $j_i' \rightarrow j_f'$ is calculated with the help of IOSA formulas modified by introducing a resonance function $R(\omega)$, the adiabaticity correction factor. This $R(\omega)$ function has the form of a Lorentz profile multiplied by the factor of detailed balance. The latter provides the relation

$$R(-\omega) = \exp(-\hbar\omega/kT)\,R(\omega).$$

This asymmetric resonance function corrected (ARC) IOS approximation gives the line coupling cross-section as

$$\sigma_1^{IOS/ARC}(j_i'j_f'l_v'; j_ij_fl_v) = \sigma_1^{IOS}(j_i'j_f'l_v'; j_ij_fl_v)R(\omega_{ii'}),$$

where $\omega_{ii'} = \hbar^{-1}[E(j_i) - E(j_i')]$.

The cross-sections for line broadening are calculated from the cross-sections for line coupling by the use of sum rules.[2]

The formalism is applied to the Q branch shape analysis of $\Pi - \Sigma$ and $\Pi - \Delta$ bands of 15 μm CO_2 mixed with He. The dynamic cross-sections Q_L found from CO_2-He interaction are used. The results of the calculation describe satisfactorily the observed Q branch evolution with pressure increase.

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F36

N_2-Broadening Coefficients in the ν_3 Band of CH_3D.

Jacques WALRAND[*], Ghislain BLANQUET[*], and Jean-Pierre BOUANICH[+].

[*] Laboratoire de Spectroscopie Moléculaire, Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles, B-5000 Namur, Belgium.
[+] Laboratoire de Physique Moléculaire et Applications, CNRS, Université de Paris-Sud, Bâtiment 350, F-91405 Orsay cedex, France.

Since monodeuterated methane has been detected in the infrared spectra of Jupiter, Saturn and Titan, accurate line parameters are needed, especially for determining the CH_3D abundance and D/H ratio in planetary atmospheres. Several authors have measured the broadening coefficients by various perturbers (N_2, Air, H_2, CH_3D) in the ν_2, ν_3 and ν_6 bands of CH_3D. The results at high resolution were obtained by direct measurements eventually corrected from the Doppler width through an empirical expression (Olivero and Longbothum [1]) derived from the Voigt profile. In the present work, nitrogen-broadened halfwidths of CH_3D have been measured for 33 lines in the ^QP and ^QR branches of the ν_3 parallel-type band by fitting the individual profile of each line with Voigt and Rautian models. These lines with J values ranging from 0 to 16 and K from 0 to 8 were recorded in the spectral range 1233-1414 cm^{-1}, using a tunable diode-laser (TDL) spectrometer.

Self-, N_2-, O_2-, and H_2- broadening coefficients of CH_3D were calculated by Tejwani and Fox[2] from the Anderson-Tsao-Curnutte (ATC) theory. Our calculations of collisional halfwidths have been performed by including in the same semi-classical theory some of the improvements proposed by Robert and Bonamy. These calculations have shown the importance of the non-electrostatic contributions in the anisotropic intermolecular potential. The results we obtained for CH_3D-N_2 are very different than those given in Ref. 2.

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F37

M_J DEPENDENCE OF COLLISIONAL TRANSITION BETWEEN FINE-STRUCTURE LEVELS OF K ($4P^2P_{J,M_J}$) ATOM

J.Kawai, K.Matsubara, T.Kokita, and H.Katô

Department of Chemistry, Faculty of Science, Kobe University,

Nada-ku, Kobe 657, Japan

M.Baba

College of Liberal Arts and Sciences, Kyoto University,

Sakyo-ku, Kyoto 606, Japan

By propagating a tunable single frequency laser beam perpendicular to an atomic beam of potassium in a magnetic field, the K atom was selectively excited to a chosen magnetic sublevel $4P^2P_{1/2,M_J}$ or $4P^2P_{3/2,M_J}$. The excited K ($4P^2P_{1/2,M_J}$ or $4P^2P_{3/2,M_J}$) atom collides with an atomic beam of He, K or Rb, propagating perpendicular both to the K ($4P^2P_{1/2,M_J}$ or $4P^2P_{3/2,M_J}$) atom beam and to the direction of the magnetic field. The excitation spectrum of the K ($7S^2P_{1/2,1/2}$ and $7S^2P_{1/2,-1/2} \leftarrow 4P^2P_{3/2,M_J}$ or $4P^2P_{1/2,M_J}$) transitions pumped by a second tunable laser propagated along the direction of the magnetic field was measured. The M_J-dependence of the collisional transition and the angular distribution of the scattered K ($4P^2P_{1/2,M_J}$ or $4P^2P_{3/2,M_J}$) were studied.

F38

SPECTRAL HOLE BURNING, RESONANT TWO PHOTON IONIZATION AND HIGH RESOLUTION DISPERSED FLUORESCENCE AS PROBE OF INTERMOLECULAR VIBRATIONS IN HYDROGEN BONDED MOLECULAR COMPLEXES

K. KLEINERMANNS*, M. SCHMITT, U. HENRICHS, CH. DEUSEN, CH. JACOBY, M. GERHARDS, W. PERL
Institut für Physikalische Chemie und Elektrochemie
Universität Düsseldorf , D-40225 Düsseldorf, Germany

Hydrogen bonded clusters of phenol with methanol and ammonia and of resorcin and catechol with methanol were examined by several laserspectroscopical techniques. With Spectral Hole Burning (SHB) the cluster ground state is depopulated persistently on the time scale of the experiment by a tunable dye laser (burn laser). After a variable time delay (400 to 800 ns) the population of the ground state level is probed by a second dye laser. If probe and burn laser share a common ground state level, the ionization signal caused by the probe laser is decreased. Because of isomer and state selectivity of spectral hole burning, the rotamers of the dihydroxybenzenes resorcin and catechol were assigned unambiguously. Clear spectroscopic evidence is presented that catechol is planar in the S_o state, but nonplanar in the S_1 state with both OH groups out of the aromatic plane. The two OH torsions are strongly coupled and the experimental torsional pattern of h_2-(d_2-) catechol is compared with a full two dimensional vibrational analysis based on an ab initio potential at the HF/6-31 G* (Gaussian 92) level. The hydrogen bond in catechol-methanol quenches the two dimensional vibrational pattern of the torsion.

For the first time all 6 intermolecular vibrations of an H-bonded cluster were observed and assigned both in the S_o- and S_1-state in case of phenol·$(CH_3OH)_1$ and several deuterated isotopomers using SHB, 1+1-REMPI and Dispersed Fluorescence. Extensive Gaussian 92/HF6-31G* geometry optimizations with normal coordinate analysis were performed for assignment of the intermolecular vibrations. The minimum energy structure is trans-linear, as for the phenol/H_2O-cluster. Anharmonic corrections were made for one bend (β_2)- and the torsion (τ)-vibration by numerical solution of the Schrödinger equation along the corresponding normal coordinate elongations. 2-dimensional calculations were performed on the ab initio torsion-bend potential surface to exhibit the degree of torsion-bend coupling. The calculations and the deuteration experiments allowed an assignment of all six intermolecular vibrations as well as several overtone and combination bands.

For phenol $(NH_3)_1$, four bands in the region of intermolecular vibrations could be assigned to the 1:1 complex by mass resolved SHB and two colour ionization just above the ionization threshold. The ab initio computed cluster structure and its normal vibrations are reported and compared to the experimental results. Anharmonic calculations were carried out for the ammonia torsion and compared to experiment.

* *9 Publications on Clusterspectroscopy 1995, available on request.*

F39

OBSERVATION OF STRONG
CORIOLIS COUPLING
IN THE IR-SPECTRUM OF AR–CO

S. König, G. Hilpert and M. Havenith

Institut für Angewandte Physik, Universität Bonn,
Wegelerstr. 8, 53115 Bonn (Germany)

Using a continuous two–dimensional jet expansion in combination with a computer controlled diode laser spectrometer, the rotation–vibration spectrum of the Ar–CO van der Waals complex has been studied in the 2157 cm^{-1} region.

47 new lines of the parallel transition from the $K_a = 1$ $(j = 1)$ ground state $(v_{CO} = 0)$ to the combination band of the CO fundamental vibration $(v_{CO} = 1)$ and the excited bending, $K_a = 1$ $(j = 2)$ state were assigned. The lower state is identical to the one found by McKellar *et al.* [1]. The excited bending, $K_a = 1$ state is located at an energy of 7.98 cm^{-1} with respect to the $K_a = 2$ $(j = 2, v_{CO} = 1)$ state. Due to a strong Coriolis interaction with a nearby $K_a = 0$ state, this band shows unusually large asymmetry splittings.

This first experimental evidence of the excited bending, $K_a = 1$ state together with the van der Waals bending mode reported in [2] should provide a sensitive test of the anisotropic part of the potential.

We will present spectroscopic results and an analysis of the observed spectra.

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F40

(Several?) Electronic States of NiCl$_2$ in the 360nm region measured at rotational resolution

G. van den Hoek
J.M. Brown

The Physical and Theoretical Chemistry Laboratory
Oxford University
South Parks Road, Oxford OX1 3QZ
United Kingdom

High resolution measurements with an experimental resolution of 0.002cm^{-1} have performed in the 360 nm band system of NiCl$_2$. Laser induced fluorescence was detected from a jet which was excited by an intra cavity doubled titanium:sapphire CW laser. Rotational resolution has been achieved and assignments lead to the determination of the rotational constants in both the electronically excited state and the ground state. The values of these constants point out that these transitions stem from the same electronic ground state as the previously measured[1] band system at 460nm.

A total of 56 different transitions are analysed. Of these transitions only a few are unperturbed. These unperturbed spectra are simulated with simple rotational formulas and with a rotational temperature of 20K. Interactions between different electronic states are probably causing the strong perturbations in most transitions. At least two different electronic states are accessible in the 360nm band system.

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F41

SPECTROSCOPY WITH THE COLOGNE TERAHERTZ SPECTROMETER UP TO FREQUENCIES OF 1.27 THZ

S.P. Belov, F. Lewen, Th. Klaus, H. Klein, E. Klisch, R. Schieder, G. Winnewisser

I. Physikalisches Institut, Universität zu Köln,
D–50937 Köln, Germany

and

E. Herbst

Departments of Physics and Astronomy, The Ohio State University,
Columbus, OH 43210

High resolution, broadband scanning spectroscopy with microwave accuracy has been extended into the terahertz region by stabilization of continuously tunable backward wave oscillators (BWOs) (1,2). The high frequency limit reached without frequency multiplication has now been extended up to 1.27 THz.

For recording terahertz radiation above 1 THz, a new detector system (QMC Instr. Ltd., U.K.) has been added to the technical setup of the spectrometer. It provides two liquid helium cooled and magnetically tuned InSb hot electron bolometers with sensitivity up to 2.5 THz and peaks at 1.3 and 2 THz. From measurements of weak CH_3CN transitions at 1.04 THz we estimate the sensitivity to be about $10^{-8}\,cm^{-1}$.

The microwave accuracy of the spectrometer in the entire submillimeter region is demonstrated by measurements of pure rotational transitions of CO between 115 and 1270 GHz. The line positions agree very well with the results obtained by tunable far infrared laser techniques (3, 4).

New measurements have been performed on the isotopomers of H_2S, the disulfane isotopomer D_2S_2, formaldehyde H_2CO, and methanol CH_3OH. These spectra, which are in part of astrophysical interest, will be presented.

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F42

GETTING THE INFORMATION YOU NEED

Jürgen Vogt, Wolfgang Hutter and Natalja Vogt

Sektion für Spektren- und Strukturdokumentation
University of Ulm, D-89069 Ulm, Germany
Internet: Juergen.Vogt@Chemie.Uni-Ulm.de

For many years the MOGADOC (MOlecular GAsphase DOCumentation) database has been a powerful tool for scientists all over the world to retrieve information about gas phase investigations. Covering both laboratory and astronomical literature it provides the user with a fast and easy access to literature and structures of molecules studied in the gas phase. So it is possible to keep track of current subjects of interest and molecules under study and to retrieve information about laboratory work and astronomical studies.

The sources used for compiling the information include "standard" journals as well as publications that are difficult to access or "grey" literature like workshops, conferences and symposia.

Currently the customer's version of this database contains over 21,400 bibliographic entries for over 6000 compounds, which gives a complete coverage of publications for electron diffraction (since 1930), microwave spectroscopy (since 1945) and molecular radioastronomy (since 1960). Recently extensive efforts are being made to include numeric structural data which, up to now, allows the user to search and display over 3000 numeric entries that include interatomic distances, bond angles and dihedral angles. The bibliographic information includes keywords characterising the contents of the article which makes it possible to select the publications of interest very conveniently.

The platform for the database is a local IBM compatible PC. Versions for both MS-DOS and Windows are available, both either on diskettes or CD-ROM.

Currently available features include (all searchable information can, of course, be displayed):

- Messenger-like command environment
- combination of search terms by usual Boolean operators and proximity operators (L), (A) and (W)
- search for bibliographic data
- search for contents of the article (hierarchical thesaurus)
- crossfiling between bibliographic and compound files
- search for compound name
- search for CAS registry number
- search for molecular formula (Hill system)
- search for element count (for C, H, N, O, P, S)
- display of structural formula and stereo drawings

F43

Direct Absorption Measurements of Ar–CO Rotational Transitions with a Supersonic Jet mm–Wave Spectrometer

M. Hepp[1], W. Jäger[2], I. Pak[1,3], and G. Winnewisser[1]

[1]*I. Physikalisches Institut, Universität zu Köln,*
50937 Köln, Germany

[2]*Department of Chemistry, University of Alberta, Edmonton, Canada*

[3]*Institute of Spectroscopy, Russian Academy of Science,*
142092, Troitzk, Moscow Region, Russia

We have constructed a pulsed supersonic jet millimeter wave spectrometer for the investigation of weakly bound complexes. Two millimeter wave synthezisers operating in the range from 50 to 80 and from 80 to 120 GHz served as radiation sources. Gas mixtures at stagnation pressures up to 5 atm. were expanded through a 0.5 mm circular nozzle into a chamber evacuated by a 250 m^3/h roots pump. The pulsed operation of the nozzle (120 Hz) produced a modulation of the absorption signal which was detected using a boxcar integrator.

The sensitivity of this direct absorption method was demonstrated by measuring several new $\Delta K_a = 1$ rotational transitions of the very weakly dipolar Ar–CO van der Waals complex.

G1

NETWORKS OF ANHARMONIC RESONANCES IN THE HIGH RESOLUTION SPECTRUM OF HCNO

Manfred Winnewisser and Sieghard Albert

Physikalisch-Chemisches Institut
Justus-Liebig-Universität Gießen
Heinrich-Buff-Ring 58
D-35392 Gießen, Germany.

Fulminic acid belongs to the class of quasilinear molecules. From the ℓ-type doublets in the microwave region up to the vibrational overtones in the near infrared region, we can now put forward extensive spectroscopic data for the isotopomers HCNO, DCNO, $H^{13}CNO$, $HC^{15}NO$, and $H^{13}C^{15}NO$. The low symmetry of the molecule and the strongly anharmonic quasilinear bending mode lead to a network of anharmonic resonances in the entire infrared region. The complex rovibrational energy level schemes of these isotopomers and the observed and analysed anharmonic interactions will be discussed. Due to the isotopic substitutions many of the Coriolis-type and/or Fermi-type resonances can be tuned and therefore yield the assignment of the dark states involved. The vibrational term value schemes to be presented were built up experimentally with the help of the Ritz combination principle or by analogy between the various isotopic species.

G2

DOUBLE-RESONANCE VIBRATIONAL OVERTONE SPECTROSCOPY
OF JET-COOLED MOLECULES USING IRLAPS DETECTION

O V. Boyarkin, L. Lubich,[a] D. S. Perry,[b] and T. R. Rizzo

Institut de chimie physiqe, Ecole Polytechnique Fédérale de Lausanne,

CH-1015 Lausanne, Switzerland

Interpreting the spectral structure of high vibrational overtone transitions in terms of the dynamics of the excited molecules requires spectral simplification to remove inhomogeneous broadening. We apply infrared-optical double resonance overtone excitation to molecules cooled in a supersonic free jet to generate simplified vibrational overtone spectra. Detection of the overtone excitation is accomplished using the recently developed technique of infrared laser-assisted photofragment spectroscopy (IRLAPS).[1] This involves selectively dissociating the vibrationally excited molecules *via* infrared multiphoton excitation using a CO_2 TEA laser and then spectroscopically detect the resulting decomposition products using laser induced fluorescence. Scanning the overtone excitation laser frequency while keeping all others fixed generates an overtone excitation spectrum of the jet-cooled molecules. Such spectra carry detailed information on the intramolecular dynamics of the highly excited molecules.

This talk will describe our recent applications of this approach to measure vibrational overtone spectra of jet-cooled CH_3OH and CF_3H.

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[a] Permanent Address: Dip. di Fisica, Università di Trento, I-38050

[b] Permanent Address: Department of Chemistry, University of Akron, Akron, Ohio 44325

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H1

GENERALIZED QUANTUM DEFECT THEORY
AT LOW ENERGIES

F.Texier and Ch.Jungen

Laboratoire Aimé Cotton

Université Paris-Sud

91405 Orsay France

The Quantum Defect Theory (QDT) [1], is usually applied to Rydberg states where a single electron in a neutral atomic or molecular system is highly excited, such that most of its probability amplitude distribution lies outside the positively charged residual atomic or molecular core. The key quantity characterising the motion of the electron outside the core is the effective principal quantum number, which is equivalent to the so-called accumulated phase.[2] Here we consider low excitation of a particle moving in an arbitrary (i.e. non Coulombic) field. A numerical procedure is developed which allows the accumulated phase to be calculated at energies lower than the first bound level, or even below the potential minimum ('strongly closed channel'). The importance of this energy region for practical applications of QDT is pointed out.

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FAST ION BEAM HIGH RESOLUTION LASER INDUCED FLUORESCENCE SPECTRUM OF $B^4\Sigma_u^-$ - $X^4\Sigma_g^-$ TRANSITION OF THE C_2^{+1}.

K. Boudjarane and M. Larzillière

Laboratoire de physique atomique et moléculaire

Département de physique, Université Laval

Québec Canada G1K 7P4.

M. Carré

Laboratoire de Spectrométrie Ionique et Moléculaire

Université Claude Bernard Lyon I

69622 Villeurbanne CEDEX, France.

We have used the laser induced fluorescence (LIF) technique on a fast ion beam to study the $B^4\Sigma_u^-$ - $X^4\Sigma_g^-$ system of C_2^+ homonuclear molecular ions. We have observed rotational lines of the (1,0) (1,1) bands by means of a Doppler tuning technique. The high resolution, due to the kinematic compression of the velocity spread, has allowed a detailed study of spin splittings and molecular constants. The observed rotational structures show that the upper $B^4\Sigma_u^-$ state is perturbed by the close lying $2^2\Pi$ electronic state. Interaction parameters are also given.

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[1]Submitted to Chem. Phys. Lett.

H3

THE ULTRA-VIOLET AND INFRA-RED SPECTRUM OF THE NCN RADICAL

K. D. Hensel, S. A. Beaton, Y. Ito and J. M. Brown
Physical and Theoretical Chemistry Laboratory
South Parks Road
Oxford
UK
OX1 3QZ

The (0,0) band of the $\tilde{A}^3\Pi_u - \tilde{X}^3\Sigma_g^-$ transition of NCN, observed previously by Herzberg and Travis[1], has been reinvestigated by means of laser-induced fluorescence in the region 30295-30465cm^{-1}.

A frequency doubled dye laser was used to record the spectrum of NCN downstream of a microwave discharge through N_2 and CF_4 in He (ref.[2]).

From the rotational analysis, improved values for the molecular constants of NCN in both states were obtained, including Λ-type doubling parameters for the $^3\Pi_u$ upper state. Futher work on the ν_2 hot bands is now in progress.

The main molecular constants obtained were

$\tilde{X}^3\Sigma_g^-$: $B_{000}'' = 0.3972458(95)\text{cm}^{-1}$ $\lambda'' = 0.79402(50)\text{cm}^{-1}$

$\tilde{A}^3\Pi_u$: $B_{000}' = 0.3966487(95)\text{cm}^{-1}$ $A' = -37.4493(38)\text{cm}^{-1}$

$$T_{000}' = 30383.8110(51)\text{cm}^{-1}$$

Using the same method of production, efforts have been made to locate the infrared spectrum of NCN in the ν_3 band region (ca. 1470cm^{-1}) (ref.[3]) using CO laser magnetic resonance (LMR). Signals have been observed, but their assignments to transitions in NCN has proved to be difficult and work is still in progress.

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H4

HYPERFINE CONSTANTS OF BrF AND IF

Holger S.P. Müller* and Michael C.L. Gerry

Department of Chemistry, The University of British Columbia

2036 Main Mall, Vancouver, B.C., Canada

V6T 1Z1

The J'-J'' = 1 - 0 rotational transitions of ^{79}BrF, ^{81}BrF, and IF have been reinvestigated in the ground and first excited vibrational states using microwave Fourier transform spectroscopy. For IF, lines were also detected in the second excited vibrational state. Bromine and iodine nuclear quadrupole coupling constants, spin-rotation constants for all nuclei, and tensor and scalar spin-spin coupling constants (S and J), have been determined along with the rotational constants. Antishielding occurs at the fluorine nucleus for both BrF and IF, as has been found earlier for ClF. The antishielding has been rationalized following a model developed for ClF.

*Present address: Jet Propulsion Laboratory 183-301,
California Institute of Technology, 4800 Oak Grove Drive,
Pasadena, CA 91109, U.S.A.

SPECTROSCOPY OF CrF: RECENT RESULTS ON THE $A^6\Sigma^+$–$X^6\Sigma^+$ AND $B^6\Pi$–$X^6\Sigma^+$ BAND SYSTEMS IN THE NEAR INFRARED.

S.Wallin, R.Koivisto and O.Launila

Department of Physics, Stockholm University
Box 6730 S-11385 Stockholm, Sweden

The electronic spectrum of the CrF radical has been recorded at high resolution (0.025 cm⁻¹) in the spectral region 7000-11700 cm⁻¹ with FTS techniques. In this region, 2 bands of the $B^6\Pi$–$X^6\Sigma^+$ system and 6 bands of the $A^6\Sigma^+$–$X^6\Sigma^+$ system are strong enough to be studied at high resolution. The origins of the excited states are located at 8115 cm⁻¹ [$B^6\Pi$(v=0)] and at 9913 cm⁻¹ [$A^6\Sigma^+$(v=0)], respectively. The line material consists of more than 15000 assigned rotational lines. Strong perturbations were observed in the $A^6\Sigma^+$ state [1,2], while no local perturbations were found in the $B^6\Pi$ state [3]. The possible causes of the $A^6\Sigma^+$ state perturbations are discussed, and the $B^6\Pi$ state is shown to be the dominating perturber. However, the $A^6\Sigma^+$(v=0) perturbation pattern appears to be too complex to be caused by $B^6\Pi$(v=3) alone, and we tentatively suggest that the perturbations not attributable to $B^6\Pi$(v=3) might be caused by a quartet state. The leading electronic configurations of the low-lying sextet states of CrF are (the metallic Cr_{3d} orbitals are put in brackets):

$X^6\Sigma^+$	...[$1\delta^2 4\pi^2$]$9\sigma^1$
$B^6\Pi$	...[$1\delta^2 4\pi^1 10\sigma^1$]$9\sigma^1$
$A^6\Sigma^+$	...[$1\delta^2 4\pi^2 10\sigma^1$]

Against this background, it appears surprising that the $B^6\Pi$–$X^6\Sigma^+$ transition has not yet been observed in the CrH radical, although the $A^6\Sigma^+$–$X^6\Sigma^+$ transition is reasonably strong in both CrH and CrF.

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H6

The ν_1 Band System of HCCCN

F. Winther, Inst. f. Phys. Chemie der Universität Kiel
D- 24098 Kiel, Deutschland
and
S. Naïm, L. Mbosei, and A. Fayt, Univ. Cath. de Louvain,
Lab. de Spectr. Mol., B-1348 Louvain-la Neuve, Belgique

The ν_1 band system of cyanoacetylene (HCCCN) has been observed with an effective resolution of 0.006 cm^{-1}. ν_1 = 3327.37085(3) cm^{-1}, B_1 = 0.15149762(2) cm^{-1}, D_1 = 1.8065(3) x 10^{-8} cm^{-1}. Several hot bands from the states ν_5 = 1, ν_6 = 1, ν_7 = 1,2 (ℓ=0 and 2), 3 (ℓ=1 and 3) and 4 (ℓ=0 and 2), ν_6 = 1 and ν_7 = 2 (ℓ=3) have also been observed and analysed. Many bands show strong local perturbations due to interactions with states which are combinations of the modes 4, 5, 6, and 7. These perturbing states are also described quantitatively and ro-vibrational constants are given.
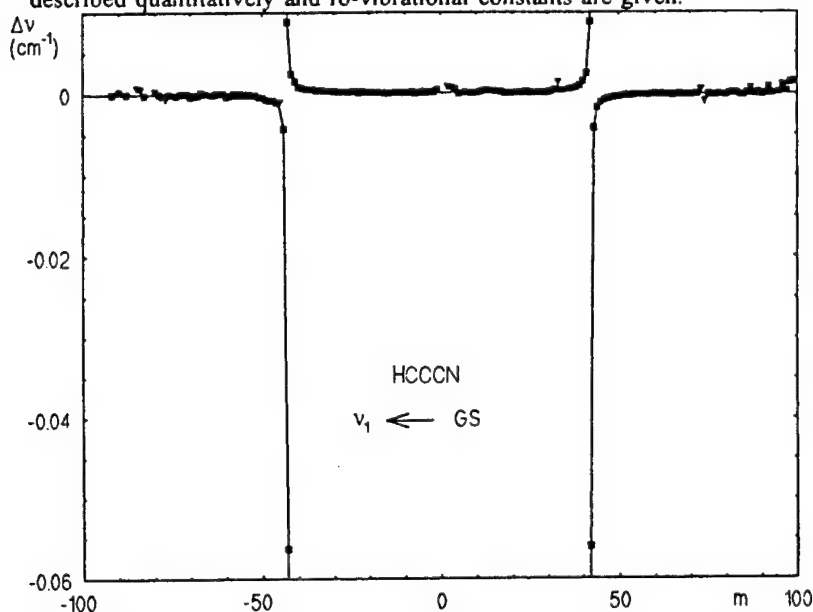
The perturbation of the ν_1 = 1 level by $\nu_4\nu_5\nu_6\nu_7$ = 1213 (ℓ=0). $\Delta\nu$ is the energy difference between calculated (lines) or observed (dots) ro-vibrational levels and corresponding unperturbed levels. (m = J+1 for R and m = - J for P branch.)

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THE B²Σ INTERACTION POTENTIAL OF LiAr
DEDUCED FROM LASERSPECTROSCOPIC DATA

R. Brühl and D. Zimmermann

Institut für Strahlungs- und Kernpyhsik

Technische Universität Berlin

Hardenbergstr. 36, D-10623 Berlin

Our previous measurements of the absorption spectrum of LiAr due to the transition $A^2\Pi \leftarrow X^2\Sigma$ /1/ have been extended to the region of the transition $B^2\Sigma \leftarrow X^2\Sigma$. The rotational structure of several vibrational bands leading to the levels v' = 1, 2 and 3 of $B^2\Sigma$ could be analyzed for both isotopomers ^{7}LiAr and ^{6}LiAr, thus allowing a determination of the vibrational numbering. For the $B^2\Sigma$ interaction potential we use a Lennard-Jones (8, 6) potential as a rough first approximation with $C_6 = 6.85 \cdot 10^6$ cm^{-1} Å^6 and $C_8 = 1.87 \cdot 10^8$ cm^{-1} Å^8 as our preliminary results, leading to a well-depth of (36 ± 3) cm^{-1} and an equilibrium distance of 6.03(10) Å. In addition, further vibrational levels of $A^2\Pi$ with v' = 9...11 have been observed, but have not been analyzed completely due to local perturbations. Up to now, our experimental data don't show any indication of an avoided crossing between $B^2\Sigma$ and $A^2\Pi_{1/2}$, being predicted by theoretical calculations.

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H8

A RE-INVESTIGATION OF THE A^2A_1 - X^2B_1 TRANSITIONS OF NH_2 AND H_2O^+ IN THE NEAR INFRARED REGION.

T. Huet, I. Hadj Bachir and J.L. Destombes

Laboratoire de Spectroscopie Hertzienne, associé au C.N.R.S.
Université des Sciences et Technologies de Lille
F-59655 Villeneuve d'Ascq cedex, France

M. Vervloet

Laboratoire de PhotoPhysique Moléculaire du C.N.R.S.
Bât. 213, Université de Paris-Sud, F-91405 Orsay cedex, France

A Titanium-Sapphire laser spectrometer was used to record the optogalvanic spectrum of NH_2 in the region 11300-14200 cm^{-1}. It was also used to record the absorption spectrum of H_2O^+, between 12000 and 13500 cm^{-1}, by applying the velocity modulation technique. The extensive rotational analysis of these spectra, added to the results of the analysis of the Fourier transform spectra of these two Renner-Teller molecules, yield to the identification of a large number of new rovibronic levels. These results will be compared to the previous works[1,2] and to the recent ab-initio calculations carried out on these two species [3,4].

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H9

PROTON REARRANGEMENT DYNAMICS AND SPECTRUM OF CH_5^+

P. R. Bunker

Steacie Institute for Molecular Sciences,

National Research Council of Canada,

Ottawa, Ontario, Canada K1A OR6.

Using the *ab initio* results of P. R. Schreiner, S.-J. Kim, H. F. Scha-effer and P. von R. Schleyer (*J. Chem. Phys*, **99**, 3716-3720, 1993) the proton rearrangement energy levels and spectrum of the CH_5^+ molecular ion are calculated. The molecule should be considered as an H_2 molecule bound at the apex of a pyramidal CH_3^+ ion with the H_2 axis perpendicular to the C_3 axis of the CH_3^+ unit. The internal rotation of the H_2 about the C_3 axis has a barrier height of 30 cm^{-1}. There is also an internal motion through a C_{2v} structure, with a barrier of 300 cm^{-1}, that makes all 120 symmetrically equivalent equilibrium structures accessible. All proton permutations are therefore feasible and the complete nuclear permutation inversion group of 240 elements is used for the symmetry classification of the energy levels.

H10

EFFECTIVE OPERATORS APPROACH FOR GLOBAL TREATMENT OF VIBRATIONAL-ROTATIONAL SPECTRA OF CARBON DIOXIDE

J.-L.Teffo

Laboratoire de Physique Moléculaire et Applications, CNRS, Université Pierre et Marie Curie, Boite 76, 4 Place Jussieu, 75252 Paris-cedex 05, France

V.I.Perevalov, O.M.Lyulin, E.I.Lobodenko and O.N.Sulakshina

Institute of Atmospheric Optics, Russian Academy of Sciences, Siberian Branch, 1 Akademicheskii av., 634055 Tomsk, Russia

The effective operators method has been applied to the global treatment of vibrational-rotational spectra of carbon dioxide. For this purpose a reduced effective Hamiltonian which contains both Fermi ($\omega_1 \approx 2\omega_2$) and Coriolis ($\omega_3 \approx \omega_1 + \omega_2$) resonance interaction terms has been suggested. The experimental values of spectroscopic constants G_v, B_v and D_v have been fitted to the parameters of this Hamiltonian. The fitted parameters have allowed us to reproduce about 15000 line frequencies of the principle isotope of CO_2 with a rms=0.016 cm^{-1}. Using the eigenfunctions of this effective Hamiltonian fittings of experimental intensity data to parameters of the effective dipole moment operator have been performed. The 15 mμ and 4.3 mμ regions have been considered. All fittings have been performed with an accuracy close to the experimental one. To check the consistency between fitted values of effective dipole moment parameters on one hand and force field and dipole moment function of Wattson and Rothman[1] on the other contact transformation calculations of effective dipole moment parameters have been performed. A satisfactory agreement between fitted and calculated values of these parameters has been obtained.

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H11

High Precision Measurement of the Dipole Moment of HOCl
by Tunable FIR Stark Spectroscopy

G. Modugno, P. De Natale, M. Bellini, M. Inguscio,

European Laboratory for Nonlinear Spectroscopy (LENS)
Depratment of Physics, University of Firenze
Largo E. Fermi 2, 50125 Firenze, Italy

G. Di Lonardi, L. Fusina,

Dipartimento di Chimica Fisica e Inorganica
Università di Bologna
Viale Risorgimento 4, 40136 Bologna, Italy

M. Godefroid and J. Vander Auwera,

Laboratoire de Chimie Physique Moléculaire C.P. 160/09
Université Libre de Bruxelles
50 avenue F. D. Roosevelt, 1050 Brussels, Belgium

Generation of coherent radiation from the difference of two CO_2 lasers in a MIM diode (TuFIR) is a unique tool for high precision far infrared spectroscopy with continuous spectral coverage in the 0.3 - 6 THz range. The intrinsic simplicity of the optical scheme allows combination with special absorption cell designs such as those required for the application of the highly intense electric fields needed for Stark spectroscopy. FIR Stark spectroscopy is very useful to determine electric dipole moments, which are important in different fields of application.

We report here on the measurement of the electric dipole moment of hypochlorous acid (HOCl), an important molecule for the chemistry of ozone in the stratosphere. The wide spectral tunability allows a determination of the dipole moment starting from two different transitions of HOCl, namely 1_{11}-0_{00} at 628 GHz and the asymmetry doublet 4_{32}-3_{21} and 4_{31}-3_{22} at 3.1 THz, using electric fields up to 5 kV/cm. The accurate frequency determination of the TuFIR spectrometer, at the level of one part in 10^8, gives a relative precision of about 10^{-3} in the determination of the μ_a component.

We will present experimental results as well as a theoretical modelling for the interpretation of the data. The model takes into account that HOCl is an asymmetric rotor, with the additional complication of a non-zero nuclear spin for chlorine, which gives rise to a rich hyperfine structure.

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H12

LINE STRENGTHS FOR HeH_2^+

M. Juřek, V.Špirko,

J.Heyrovský Institute of Physical Chemistry
Academy of Sciences of the Czech Republic
Dolejškova 3, 18223 Prague 8, Czech Republic

and W.P.Kraemer

Max-Planck-Institute of Astrophysics,
Postfach 1523, D-85740 Garching, Germany

All bound rotation-vibration energy levels and the line strength for all bound-bound transitions in HeH_2^+ are evaluated from recently determined ab initio potential energy and electric dipole moment surfaces[1] using the full dimensional Sutcliffe-Tennyson Hamiltonian[2]. The calculations show that HeH_2^+ has rather strong absorption lines in the infrared region and they thus demonstrate that it should be possible to detect its yet unobserved spectrum.

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H13

INTENSITIES MEASUREMENTS OF OZONE LINES IN THE v_3 BAND BY TUNABLE DIODE LASER SPECTROMETRY

M.R. DE BACKER, D. COURTOIS

G.S.M.A., U.A. CNRS D 1434

Faculté des Sciences

BP 347 - 51062 REIMS Cédex - France

Because of the important part played by the ozone in the Earth's atmosphere, the vibrational-rotational spectra of $^{16}O_3$ are the subject of numerous high resolution studies.

A tunable diode laser spectrometer has been used at the Reims GSMA laboratory to record high resolution O_3 spectra. The recorded ozone lines belong to the v_3 band, the strongest infrared band lying in the atmospheric window at 10 μm. Therefore accurate spectroscopic data are expected in this region.

Valid measurements of ozone intensities lead to accurate knowledge of ozone amount. This has been achieved by double checking the ozone pressure with a precise baratron gauge and with ultra-violet techniques.

The ozone intensities are presented and discussed here.

H14

THE ONSET OF VIBRONIC CHAOS IN NO_2
BETWEEN 10000 CM^{-1} AND 17000 CM^{-1}

M.Barthélémy, A.Delon, R.Jost
LCMI/CNRS BP 166 38042 Grenoble Cedex 9
J.Liévin
Chimie Physique Moléculaire CP.160/09 ULB 1050
Bruxelles Belgique

The origin of vibronic chaos in NO_2 lies in an conical intersection between the Potential Energy Surfaces (PES) of the electronic ground state, $\tilde{X}\,^2A_1$, and the first electronic excited state, $\tilde{A}\,^2B_2$, which induces strong vibronic couplings between the vibrational levels of these two states above 17000 cm^{-1}. We present the different experimental tools and theoritical approaches which allow to investigate the onset of vibronic couplings in NO_2 above 10000 cm^{-1}.

-The mixings between the vibrational levels of the $\tilde{X}\,^2A_1$ and those of $\tilde{A}\,^2B_2$ decrease statistically with decreasing energy. It implies that some $^2B_2$ vibronic levels (the highly excited levels of $\tilde{X}\,^2A_1$) are practically not observable. This must be compared to the behavior above 17000 cm^{-1} where more than 96% of the $^2B_2$ vibronic levels have been observed.

-Laser Induced Dispersed Fluorescence Spectroscopy allowed to assign 70 levels below 17000 cm^{-1} with vibrational quantum numbers in $\tilde{A}\,^2B_2$.

-The study of lifetimes brings information about the relative weights of $\tilde{X}\,^2A_1$ and $\tilde{A}\,^2B_2$ in each particular $^2B_2$ vibronic state.

-*Ab initio* calculations of the PES give a tractable expression of the vibronic matrix elements in the diabatic basis. This matrix element can be used in order to reproduce the observed structure of the vibronic spectrum in both the intermediate energy range and in the chaotic energy range.

H15

ROVIBRONIC INTERACTIONS IN NO$_2$

Jesper Nygård, Antoine Delon and Remy Jost
Laboratoire des Champs Magnetiques Intenses,
CNRS, B.P. 166, F-38042 Grenoble Cedex 9, France

The visible spectrum of NO$_2$ shows a high degree of complexity. One remarkable feature is the irregular rotational structure of the vibronic bands, due to rovibronic (spin-rotation) interactions which couple rotational levels belonging to different vibronic bands.

In order to simplify the observed spectrum we have performed LIF measurements using a supersonic jet, which reduces the rotational temperature to a few Kelvin, so only the lowest rotational levels of each band appear. We present a statistical analysis of several hundred bands and show that the average rovibronic matrix element is roughly independent of the energy. Consequently, the increasing complexity of the rovibronic spectrum with energy should be attributed solely to the increasing density of states.

We have developed a random-matrix based model that predicts statistical properties of the low-temperature spectrum, taking into account the rovibronic interactions. The model is currently being extended in several directions:

(i) towards higher energy in order to predict spectral properties of NO$_2$ just below the dissociation limit – is rovibronic chaos present?

(ii) the inclusion of higher rotational levels in the calculations simulates the spectrum at higher temperatures. Hopefully, this will lead to a better understanding of the extreme complexity of the room temperature spectrum.

(iii) by including the Zeeman effect, we can simulate the rich anticrossing structures which we observe experimentally using jets in high magnetic fields (see Pasinski *et al*).

H16

EVOLUTIONS OF ROVIBRONIC LEVELS OF JET COOLED NO$_2$ IN HIGH MAGNETIC FIELD.

A. Pasinski[1,2], F. Bylicki[2], A. Delon[1], R. Jost[1]

[1] LCMI CNRS/MPI

BP 166, 25, av. des Martyrs

38042 Grenoble cedex 09, France

[2] I.F. UMK

ul. Grudziadzka 5/7

87-100 Torun, Poland

In the visible range, the room temperature NO$_2$ spectrum is very difficult to analyze due to vibronic and rovibronic interactions. High density of vibrational levels and vibronic interactions between them induces chaotic behaviour of vibronic levels above 17000 cm^{-1}. In addition the spectrum displays some rovibronic "extra" lines induced by rovibronic interactions. We decide to study these rovibronic interactions via Zeeman Anticrossing Spectroscopy experiment. The jet cooled NO$_2$ molecules (T$_{rot}$ ≤ 3K) are excited with a laser in a single rovibronic level (bright level) and we observed the fluorescence (L.I.F.). Evolution of sublevel in magnetic field let us to observe the Zeeman effect up to 14 teslas and in addition the interaction between bright levels and dark levels via anticrossings with the selection rule : $\Delta M = 0$ where $M = M_s + M_i + M_n$.

As results, we get precise values of Lande factor (for field range 0 - 14 teslas), we determine values of rovibronic matrix elements, define quantum numbers for perturbers and find correlations occurring between rovibronic levels belonging to the same pair of bright and dark vibronic levels.

H17

IRREDUCIBLE VIBRATIONAL OPERATORS ADAPTED TO COMPLEX BAND SYSTEMS OF POLYATOMIC MOLECULES. ASSOCIATED ALGORITHMS AND PROGRAMS. APPLICATION TO THE T_D, O_H AND C_3V GROUPS.

Nikitin A.[1], Champion J.P.[2], Tyuterev Vl.G.[3]

(1) Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 634055 Tomsk, Russia.
(2) Laboratoire de Physique URA CNRS 1796, Université de Bourgogne, 6 Boulevard Gabriel, 21000 Dijon, France.
(3) GSMA, URA CNRS D 1434, Faculté des Sciences, BP 347, 51062 Reims, France.

We report a method for the construction of vibrational operators particuliarly suitable for the investigation of highly excited states within complex interacting band systems of polyatomic molecules.

Such operators are characterized by their ability to be used for an arbitrary number of interacting vibrational modes and for arbitrarily high polyads. The method allows to apply efficiently recursive algorithms to calculate commutators and matrix elements required to set up Hamiltonian and transition matrices, as well as to study their mathematical properties.

A vibrational operator is constructed in several steps according to two main features: (i) The permutation group is used to classify the symmetrized power of irreducible representations of the point group. (ii) The coupling of all vibrational modes is organized as a balanced binary tree.

Programs based on this algorithm have been written, tested by comparison with existing codes relating to the T_d group, and applied to C_3v molecules.

The study of hot band systems of CH_3D will be presented as an illustration.

H18

PRECISE STUDY OF $2\nu_5$ HYBRID BAND OF CHD_3

O.N. Ulenikov

Tomsk State University, Tomsk, 634050, RUSSIA

S. Alanko, M. Koivusaari, and R. Anttila

Department of Physical Sciences, University of Oulu, FINLAND

High resolution spectrum of CHD_3 was recorded on the Bruker IFS 120HR Fourier transform spectrometer (Oulu) and analyzed in the region of hybrid $2\nu_5$ band, 2450 - 2810 cm^{-1}. As compared to usual nonhybrid perpendicular bands, the E-type subband of the $2\nu_5$ band shows anomalously large A_1 - A_2 splittings of energy levels $(J,K=2,A_{1,2})$. They are more than 10 times larger than the corresponding splittings of energy levels $(J,K=1,A_{1,2})$ having the same values of quantum number J.

To understand the complicated picture of the recorded spectrum the Coriolis resonance interactions of the types $J_{\pm}J_z q_{\mp}^2$, $J_{\pm}^2 q_{\pm}^2$, $J_{\pm}^2 J^2 q_{\pm}^2$, and $J_{\pm}^2 J_z^2 q_{\pm}^2$ between A_1 and E subbands were taken into account. As a result 558 energy levels with $J_{max} = 17$ and $K_{max} = 17$ obtained from experimental data (except levels $(J,K=3,A_{1,2})$ of the A_1-type vibrational subband) were reproduced theoretically with mean differencies between calculated and experimental values 2.7×10^{-4} cm^{-1} (for large values of J and K differences between calculated and experimental energy levels can go up to 20×10^{-4} cm^{-1}).

Exceptionally large splittings between $(J,K=3,A_1)$ and $(J,K=3,A_2)$ energy levels are satisfactorily explained by the used model of Hamiltonian, but they are not reproduced with the same accuracy as the other energy levels. For $J \leq 8$ the prediction accuracy is practically the same as for the other states but for $J \geq 9$ it begins to decrease and for $J = 16$ the difference is increased up to 0.04 cm^{-1}. Apparently some other types of resonance interactions (e.q., $\sim J_{\pm}^3$) should be taken into account.

H19

HIGH RESOLUTION STUDY OF THE IR SPECTRUM OF PF_3 MOLECULE BETWEEN 1150 AND 1400 cm^{-1} .

R.SEBIHI , H.NAJIB , N.BEN SARI - ZIZI
Laboratoire de Spectronomie physique appliquée , Faculté des Sciences , Université Mohammed V , B.P. 1014 , Rabat (Agdal) - Maroc

This range has been recorded by H . BÜRGER in Wuppertal (Germany) on his F.T. Brüker interferometer with a resolution about 3.10^{-3} cm^{-1}. It contains combination bands like $\nu_1 + \nu_2$ (1377cm^{-1}) or $\nu_1 + \nu_4^{\pm1}$ (1238 cm^{-1}) and both components of $\nu_3 + \nu_4$ which are intermixed around 1205 cm^{-1} . None of these bands has been studied before .

The assignments through the combination differences relationships have been easy for the $\nu_1 + \nu_2$ parallel band and not very difficult for the $\nu_1 + \nu_4^{\pm1}$ perpendicular band (K and J reach 50 for the two bands) which overlaps at low frequencies with $\nu_3 + \nu_4$. But it was hard to distinguish between the $A_1 + A_2$ and E components of $\nu_3 + \nu_4$ because the region between 1190 and 1220 cm^{-1} revealed to be very crowded . This is due to the fact that their centers are too close (only 0.2 cm^{-1}) and their $|A\zeta_{eff}|$ are too small (respectively 0.167 and 0.033 cm^{-1}) . Fortunately the strong $^{R}Q_0$ branch played a key part in solving this problem . It triggered the assignments of the sub-bands with K. $\Delta K= -3$ to -27 and $K\Delta K= 0$ to15 (about 250 lines with Jmax # 30) for $\nu_3^{\pm1} + \nu_4^{\pm1}$ E , whose intensity is about half that of the $\nu_3^{\pm1} + \nu_4^{\mp1}$ $A_1 + A_2$. For this last component the^{Q}Q branches are very week but we have identified the sub-bands with K$^-$ = 0 to 33 from the strong $^{Q}R^-_K(J)$ lines and K$^+$ = 6 to 42 from the strong $^{Q}P^+_K(J)$ lines (about 900 lines with Jmax # 45) . The assignments of $\nu_3^{\pm1} + \nu_4^{\pm1}$ E will certainly extend at least until K # 36 .

Since a Coriolis interaction exists between ν_1 and ν_3 fundamental bands [1], we must find it again between $\nu_1 + \nu_2$ and $\nu_2 + \nu_3$ (centered about 1345 cm^{-1} but no line observed) or between $\nu_1 + \nu_4$ and both components of $\nu_3 + \nu_4$.
- For $\nu_1 + \nu_2$, several trials (with the coupling term and all the $\nu_2 + \nu_3$ parameters constrained except the band center) have always increased the r.m.s deviation from 0.62 $.10^{-3}$ cm^{-1} value which was obtained with classical least squares calculation over 1815 lines . Therefore this interaction could not be reached far from the crossing which occurs near K = 100 .
- For $\nu_1 + \nu_4$, a provisional fit , taking into account only the l(2,2) resonance due to ν_4 mode , gave a r.m.s deviation of $3.5.10^{-3}$ cm^{-1} over1531 lines .
- After finishing the assignments of $\nu_3 + \nu_4$ the next step will be the modelisation of matrix interaction with at least l(2,2) , l vibrational and Coriolis resonances between all the lines of $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$.

(1) see the corresponding poster .

H20

"RITZ" ANALYSIS OF THE FT-IR SPECTRUM OF

^{13}CH$_3$OH FROM 25 TO 350 CM^{-1}

Giovanni Moruzzi
Dipartimento di Fisica dell'Università di Pisa, Piazza Torricelli 2
I-56126 Pisa, Italy

J.C.S. Moraes
Departamento de Física e Química, UNESP
15.385-000 Ilha Solteira-SP, Brazil

B.P. Winnewisser and M. Winnewisser
Physikalisch-Chemisches Institut der Justus-Liebig-Universität Giessen
Heinrich-Buff-Ring 58, D-35392 Giessen, Germany

We have investigated the high-resolution (FWHM $= 1.5 \times 10^{-3}$ cm^{-1}) Fourier Transform Spectrum of ^{13}CH$_3$OH between 25 and 350 cm^{-1}. The work was started with an assignment program package based on a Taylor series expansion of the energy levels[1]. Subsequently the work was continued with the new "Ritz" program[2], that allowed us to assign also perturbed level sequences which could not be fitted by Taylor expansions. Altogether, 14950 lines have been assigned, and the energies of 1409 levels of A symmetry and 2347 levels of E symmetry have been evaluated. All assigned lines presented here correspond to transitions involving torsionally excited levels within the ground vibrational state. A comparison with the energy level values of the parent species ^{12}CH$_3$OH is presented. Taylor expansion coefficients for evaluating the energies of the levels involved in the transitions are also given. "Forbidden" $\Delta K = 2$ and 3 transitions, induced by state mixings, have been observed and are discussed.

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H21

SPECTROSCOPY OF THE GROUND AND EXCITED ELECTRONIC STATES OF IrF$_6$

V. Boudon and M. Rotger

Laboratoire de Physique de l'Université de Bourgogne,

U.R.A. C.N.R.S. n° 1796

6 bd. Gabriel, 21000 Dijon, France.

Firstly, we present some low resolution spectra, showing the five lower excited electronic states of IrF$_6$. These were obtained using CARY 1E/5E visible-NIR spectrophotometers. They concern the $a(G'_g)$, $b(G'_g)$, $c(E'_{1g})$ states in the 6000–10000 cm^{-1} region and the $d(E'_{2g})$ and $e(G'_g)$ states in the 12000–17000 cm^{-1} one. We also show spontaneous Raman scattering spectra of the $X(G'_g)$ ground state, between 100 and 1000 cm^{-1}. All these data were recorded at ambiant and higher temperature (sample pressure $\geq$ 250 torrs) and at a resolution of 1–2 cm^{-1} in the best cases. New values of electronic origins, vibrational wavenumbers and vibronic parameters are derived.

Secondly, we expose an attempt of high resolution spectroscopy on this molecule which is presently in progress. This is a multipass absorption experiment (at least 20 passes, i.e. a pathlength $\geq$ 8 m) concerning the $e + \nu_3 \longleftarrow X$ transition around 15850 cm^{-1} ; it uses a continuous tunable ring dye (DCM) laser and the gas pressure is maintained below 1 torr by a cooling system ($-50°$C with a Peltier effect with its hot face cooled by a refrigerating fluid circulation). Here, the resolution is $\sim 10^{-4}$ cm^{-1}.

H22

ALGEBRAIC TREATMENT OF BENDING MODES OF TETRAHEDRAL MOLECULES THROUGH THE CHAIN

$$U(6) \supset U(5) \supset U(3) \times U(2) \supset SO(3) \times SO(2) \supset SO(2)' \times SO(2)''.$$

V.BOUJUT and F.MICHELOT

Laboratoire de Physique de l'Université de Bourgogne.

U.R.A. C.N.R.S. n° 1796

6 bd. Gabriel, 21000 Dijon. France.

We introduce a special algebraic chain which seems to be the most appropriate one for the description of bending modes of most tetrahedral molecules (like SiH_4, CH_4, SnH_4, ...).In first approximation the vibrational spectrum is given through the first invariants operators associated with this chain. Greater precision requires the introduction of additional operators: we indicate how these may be built within the algebraic chain.Some results will be given for the Silane molecule for which predictions for highly excited states have been made.

H23

INTRAMOLECULAR POTENTIAL FUNCTION OF METHANE MOLECULE AS THE RESULT OF GLOBAL FIT ITS HIGH-RESOLUTION VIBRATION-ROTATION SPECTRA

O.N.Ulenikov

Laboratory of Molecular Spectroscopy, Physics Department, Tomsk State University, Tomsk, 634050, RUSSIA

R.N.Tolchenov

Laboratory of Spectroscopy, Siberian Institute of Physics, Tomsk, 634050, RUSSIA

Method was derived which gives possibility to obtaine intramolecular potential function of methane molecule directly from experimental data on high resolution vibration-rotation spectra. As the initial information experimental data on ~40 vibration-rotation bands of CH_2D_2 and ~15 bands of CH_4 molecules were used. Presence of very strong Fermi interactions between some bands in CH_2D_2 molecule gave possibility to determine correctly some force constants which have not been obtained correctly in earlier semiempirical analyses. To put the test correctnicy of determined intramolecular force field line positions of other methane isotopic speciese were calculated and compared with corresponding experimental data.

H24

TORSION-ROTATIONAL HAMILTONIAN OF A NONRIGID MOLECULE
WITH TWO NONEQUIVALENT TOPS WITH A COMMON AXIS OF ROTATION

A.V.BURENIN

Institute of Applied Physics, Russian Academy of Sciences,
46 Uljanov Street, 603600 Nizhny Novgorod, Russia

The present work deals with a class of nonrigid molecules of the CH_3BF_2 type with one symmetrical and one asymmetrical tops having a common axis of rotation. Other examples of these molecules are CH_3NO_2 and $CH_3C_6H_4F$. In molecules of this type internal rotation of the two tops takes place through a low potential barrier [1] and leads to interchange type mixing [2] of six independent equilibrium configurations. The configurational degeneracy in the energy spectrum can conveniently be described by the notion of the coordinate spin of the molecule [3]. The use of this spin in the frames of the analysis of the symmetry properties of the intramolecular motion based on the concept of a chain of symmetry groups [2] enables one to easily obtain a complete expression for the effective operator of any physical value characterizing the molecule with account of the configurational degeneracy in the arbitrary order of the perturbation theory in the form of the Taylor series in dynamic variables. This approach in the case of interchange transitions was first employed in [4], which permitted to contsruct for the CH_3OH molecule with one symmetrical top a torsion-rotational Hamiltonian which did not explicitly contain torsion coordinate operators, and, thus, even in lower orders of the perturbation theory it had a simpler form compared to its ealier used variants. Here we are considered the generalization of this construction for the class of nonrigid molecules of the above mentioned type with two nonequivalent tops.

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H25

Internal Rotation and Low-Energy Skeletal Vibrations in Acetone

Z. DUTKIEWICZ AND J. KOPUT

Dept. Chemistry, Adam Mickiewicz University, Poznań, Poland

The theory of internal rotation in acetone, CH_3COCH_3, has been extended taking into account the two low-energy skeletal vibrations: the in-plane CCC bending mode (385 cm^{-1}) and the out-of-plane CO wagging mode (484 cm^{-1}). The vibration-torsion-rotation Hamiltonian was developed, and symmetry properties were discussed.

The potential energy surface of internal rotation of the two methyl groups and the skeletal bending modes in question was determined in *ab initio* calculations using the Møller-Plesset method, up to full fourth-order (MP2-MP4), and the correlation-consistent cc-pVDZ and cc-pVTZ basis sets. The energy levels and wave functions were calculated variationally using an approximate, six-dimensional Hamiltonian, which describes the molecule bending at the carbonyl C atom, internally rotating about the CC bonds, and rotating in space. Coupling between internal rotation and the skeletal bending modes, via the kinetic and potential energy terms, has been discussed.

H26

STABILIZATION OF INTERMEDIATE INERTIAL AXIS OF ASYMMETRIC TOP MOLECULE BY ORBITING RYDBERG ELECTRON

I. M. PAVLICHENKOV

Russian National Center "Kurchatov Institute",
123182 Moscow, Russia.

It is common knowledge that the rotation of a rigid top around the intermediate inertia axis is unstable. A small deviation from this state takes the system away from such rotational regime. This is not the case if a system has additional degrees of freedom apart from rotational ones. An example of this is the Kapitza pendulum [1]. Another analogy is the new intriguing discovery in planetary astronomy where it has been shown that the Moon stabilizes the chaotic wobble of the Earth's rotational axis, which is unstable due to orbital coupling with other planets [2]. We have shown that an orbiting electron stabilizes the rotation of an asymmetric top molecule around the intermediate moment of inertia axis [3]. The stabilization is a result of the anisotropic electron-core interaction. The region of stabilization, the classical and quantum precessional motion around the intermediate axis have been found. The predicted phenomenon may be identified in experimental one-electron Rydberg spectra of asymmetric top molecules by studying the lowest levels of rotational multiplets. The unusual rotation manifests itself in the specific set of inversion doublets and in the characteristic dip in the dependence of these levels energy on the total angular momentum quantum number J.

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H27

$^{12}\text{CD}_3\text{F}$ AND $^{13}\text{CD}_3\text{F}$: COMBINED ANALYSIS OF THE ROTATIONAL AND INFRARED SPECTRA OF FOUR INTERACTING BANDS $v_2(A_1)$, $v_3(A_1)$, $v_5(E)$, AND $v_6(E)$

Ilona Merke and Jean Demaison

Laboratoire de Spectroscopie Hertzienne, URA CNRS 249, Universite de

Lille, F-59655 Villeneuve d'Ascq Cedex, France

Juha Lummila and Lauri Halonen

Laboratory of Physical Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1),

FIN-00014 University of Helsinki, Finland

Methylfluoride is spectroscopically a well studied molecule partly due to its lasing properties. We have measured rotational spectra of $^{12}\text{CD}_3\text{F}$ and $^{13}\text{CD}_3\text{F}$ under 300 GHz with a computer controlled millimeter-wave spectrometer using superheterodyne detection. In the region 340 to 470 GHz spectra were recorded with a source modulated spectrometer using a phase-locked submillimeter-wave backward-wave oscillator and a He-cooled bolometer detection. High resolution infrared spectra in the region 800 - 1350 cm^{-1} were recorded in the University of Oulu.

Due to the strong vibration-rotation interactions, the rotational spectra of the upper states and the infrared spectra have been analyzed with a model which treats simultaneously the four fundamentals. The observation of many normally forbidden transitions have allowed the determination of the ground state constants A_0 and D_{K0} for both isotopic species. As a result of the least squares fits 60 excited state and 9 ground state parameters were determined in both cases. Altogether 4390 infrared and 97 submillimeter-wave upper state transitions have been assigned for $^{13}\text{CD}_3\text{F}$ and 4270 infrared and 132 submillimeter-wave upper state transitions for $^{12}\text{CD}_3\text{F}$. Standard deviations of the least squares fits were 0.9×10^{-5} cm^{-1} and 2.2×10^{-5} cm^{-1}, respectively.

H28

CLASSICAL AND QUANTUM PHASE SPACES FOR A MOLECULE WITH INTERNAL ROTATION

Juan Ortigoso[a] and Jon T. Hougen[b]

[a]Instituto de Estructura de la Materia, C.S.I.C., Serrano 119, Madrid 28006, Spain
[b]Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

We have been exploring the use of analytical methods based on classical mechanics to understand the torsion-rotation energy level structure of methyl rotor molecules. We described earlier[1] the use of unquantized and semi-classically quantized trajectories on rotational energy surfaces[2] to treat torsion-rotation levels well below the barrier, an energy regime in which each rotational energy surface can be considered separately.

Above the barrier adiabatic separation of rotation and torsion breaks down, so that various rotational energy surfaces can touch each other, and a procedure based on isolated rotational energy surfaces is no longer valid. Also, destruction of all good quantum numbers other than the total energy and total angular momentum (associated at the most elemental level with eigenvector labeling problems) may arise because of the existence of classically chaotic regions. Following a suggestion by W. Reinhardt, we have used classical treatments of four-dimensional phase space from the literature to construct Poincaré surfaces-of-section for torsion-rotation energies above the barrier. Preliminary results suggest that classically chaotic regions appear at unexpectedly low energies for the acetaldehyde torsion-rotation problem. We are presently attempting to make a connection between our classical and quantum mechanical results using "coherent states."

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H29

ANHARMONICITY CONSTANTS OF BENZENE:
CARS SPECTRA OF CH- AND CD-STRETCH BANDS OF
C_6H_6, C_6D_6, s-$C_6H_3D_3$, o-, m-, p-$C_6H_4D_2$, C_6HD_5

T. Mangold and H.W. Schrötter
Sektion Physik der LMU München, Schellingstr. 4,
D-80799 München, Germany

The CARS spectra of benzene[1] and s-trideuterobenzene[2,3] were investigated previously with our cw-CARS spectrometer[4,5]. In a new series of measurements the spectra of the CH- and CD-streching vibrations of several isotopomers of benzene (C_6H_6, C_6D_6, 1,3,5-$C_6H_3D_3$, 1,2-$C_6H_4D_2$, 1,3-$C_6H_4D_2$, 1,4-$C_6H_4D_2$, and C_6HD_5) were recorded. For C_6H_6 and C_6D_6 the spectra could be simulated to confirm the values of anharmonicity constants determined from the resolved hot bands (C_6H_6: $x_{1,20} = -0.23$ cm^{-1}, $x_{1,18} = -2.62$ cm^{-1}; C_6D_6: $x_{1,20} = -0.20$ cm^{-1}). In the case of 1,3,5-$C_6H_3D_3$ the earlier results[2,3] were confirmed. The spectra of the di-deuterated benzenes also show numerous hot bands, but no clear assignment was possible so far. The profile of the CD-band of the penta-deuterated benzene shows a complicated structure.

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H30

THE ROTATIONAL SPECTRUM OF ETHYLARSINE

P. Drean*†, J. C. López*, J. L. Alonso* and J. Demaison†
*Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain and †Laboratoire de Spectroscopie Hertzienne, URA CNRS 249, Université de Lille I, F-59655 Villeneuve d'Ascq, France

The rotational spectra of trans- and gauche-ethylarsine have been investigated in the frequency region 12-200 Ghz.. For the trans form a- and c-type spectra have been observed. Rotational, centrifugal distortion and quadrupole coupling constants have been obtained from the analysis of spectra.

For the gauche form a- and b-type spectra have been observed. The b-type lines and some of the a-type lines show a doubling due to the interconversion between the two equivalent gauche conformers through rotation about C-As axis. A two state hamiltonian including a-type Coriolis coupling and quadrupole coupling terms has been used to analyze the spectrum. Preliminary results show that these states are only about 6 Mhz appart. The χ_{ab} off-diagonal quadrupole coupling tensor element for both states as well as the matrix elements $<0/\chi_{bc}/1>$ and $<0/\chi_{ac}/1>$ have been determined. For the $10_{1,9} \leftarrow 9_{2,8}$ transition a further doubling has been observed by FT-MW which can be attributed to the CH_3 internal rotation or to the AsH_2 inversion.

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^{33}S- Nuclear Quadrupole Coupling Constants determined by Molecular Beam Fourier Transform Microwave Spectroscopy - A Comparative Study -

U. Kretschmer, H. Hartwig, N. Hansen, and H. Dreizler

Institut für Physikalische Chemie, Christian-Albrechts-Universität Kiel,

D-24098 Kiel, Germany

The ^{33}S isotopomer has a low natural abundance of only 0.76%. Therefore only a few investigations on the ^{33}S nuclear quadrupole coupling were done yet. Due to the high resolution and sensitivity of our Molecular Beam Fourier Transform Microwave Spectrometer (MB-FTMW) it is now possible to record the rotational spectra of ^{33}S containing molecules in natural abundance. We present the results of our studies on thiophene, thiazole, isothiazole, dimethyldisulfide, dimethylsulfoxide, dimethylsulfide, and methylthiocyanat. For most of them we determined the complete quadrupole coupling tensor by an exact calculation of the hamiltonian matrix for each total quantum number F.

The nuclear quadrupole coupling can be used as a probe of the charge distribution around the coupling nucleus. The comparison of the coupling constants shows clearly the influence of the electron delocalisation in the aromatic rings of thiophene and thiazole.

H32

Characterization of the Monohalogenophosphanes by High Resolution Infrared and Millimeterwave Spectroscopies.

M. PAPLEWSKI, P. DRÉAN AND J. DEMAISON
Laboratoire de Spectroscopie Hertzienne, associé au CNRS, Bât. P5,
Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France.

H. BÜRGER AND H. BECKERS
Anorganische Chemie, FB9, Universität-Gesamhoschschule, D 42097
Wuppertal, Germany

The new molecules PH_2X (X = F, Cl, Br, and I) were prepared in the gas phase. These short-lived species cannot be isolated. PH_2F, PH_2Cl (1) and PH_2I were identified and characterized by low and high resolution FTIR spectroscopy. Most of the fundamental bands were observed. In the high resolution spectra, the rotational J and K structure of bands typical of near prolate asymmetric rotors were resolved. The millimeterwave spectra of these molecules as well as their isotopomers PD_2F and PD_2Cl were recorded at pressures ≤ 0.05 mbar in the frequency range 74-470 GHz.

Ground state parameters have been obtained by a combined fit of the millimeterwave data and the infrared ground state combination differences.

PH_2Br is the most unstable molecule of the PH_2X series. Up to date its detection by millimeterwave spectroscopy is the first report on this molecule. Its rotational constants are in agreement with their ab initio prediction.

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H33

MODELING OF THE TEMPERATURE DEPENDENCE IN THE ν_5 $^RQ_0$-BRANCH ABSORPTION OF CH_3 Cl.

Fr. Frichot[*], J.M. Hartmann[**] and N. Lacome[*]

[*]Laboratoire de Spectrochimie Moléculaire, URA CNRS 508, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris cedex 05, France

[**]Laboratoire de Physique Moléculaire et Applications, UPR CNRS 136, Université Paris Sud, Bâtiment 350, 91405 Orsay cedex, France

The simple approach developed in two previous papers[1,2] for modeling spectral absorption by Q branches was applied to the ν_5 $^RQ_0$ branch of CH_3Cl perturbed by N_2.

Spectra were recorded with a Fourier transform (Bruker IFS 120 HR) spectrometer under a resolution of 0.016 cm^{-1}.

The optical pathlength was equal to 85 cm. Various total pressures ranging from 400 to 1000 mbar were used for four different temperatures (296-260-225-195 K).

From the only knowledge of the branch intensity, satisfactory prediction of pressure, temperature and wavenumber dependences of absorption is obtained with only six parameters.

[1]J.M. Hartmann, C. Boulet, M. Margottin-Maclou, F.Rachet, B. Khalil, F. Thibault and J. Boissoles, J.Q.S.R.T., under press.

[2]J.M. Hartmann, J.P. Bouanich, C. Boulet, Gh. Blanquet, J. Walrand and N. Lacome, J.Q.S.R.T., under press.

H34

THE CALCULATION OF SPECTRAL LINESHAPES IN PRESENCE OF COLLISIONAL COUPLING

S. Belli, G. Buffa, and O. Tarrini

Dipartimento di Fisica dell'Università,
Piazza Torricelli 2, I-56126 Pisa, Italy

The calculation of spectral lineshapes in presence of collisional coupling effects raises two main problems. First, the full relaxation matrix $\Gamma_{\ell\ell'}$ must be calculated, including off-diagonal terms in the space of the lines ℓ. Second, in order to derive the spectral absorpion at frequency ν, the matrix $\nu - \nu_\ell - i\Gamma_{\ell\ell'}$ must be diagonalized, which has the dimensionality of the number of lines connected by line coupling effects.

For the first problem we present a treatment allowing to extend to the entire relaxation matrix $\Gamma_{\ell\ell'}$ the semiclassical impact models commonly used for the linewidth terms $\Gamma_{\ell\ell}$.

For the second problem we present two different approximations which can be used in different pressure ranges and are convenient when the dimensionality of the space of the lines involved is so large that a digonalization of $\nu - \nu_\ell - i\Gamma_{\ell\ell'}$ is not practicable. Moreover, we show that the lineshape may be exactly described resorting to effective lines and avoiding the repetition of the diagonalization process for every frequency ν used to plot the lineshape.

Practical examples are shown. The reliabilty of the different approximations is tested and compared to other commomly used models.

H35

Model band shape with varied branch coupling for atmospheric applications.

M. V. Tonkov, N. N. Filippov, Yu. M. Timofeyev, and A. V. Polyakov
Institute of Physics, St.Petersburg University,
Peterhof, 198904 St.Petersburg, Russia

A new empirical method for calculating infrared band shapes taking into account the line mixing effect is proposed. In this method the strong collision model[1] with weakened interbranch coupling is used.

The rotational relaxation matrix necessary for calculations is modelled as a linear combination of two matrices: the matrix of strong collisions Γ^{SC} and the matrix used in the isolated branches model Γ^{IB}.[1] The resulting matrix of varied coupling (VC) between branches Γ^{VC} is defined by

$$\Gamma^{VC} = C_b \Gamma^{SC} + (1 - C_b)\Gamma^{IB}$$

The band shape expression can be obtained either by the direct matrix inversion of a resolvent equation with rotational relaxation matrix Γ^{VC} or by using the memory function formalism. The latter method is applied in our work. The matrix Γ^{VC} makes it possible to derive an analytical expression for vibration-rotation band shapes. This VC shape can be obtained without making approximations similar to those used in the Rosenkranz shape formulation.

Apart from the conventional set of spectral line parameters one needs only one additional parameter to take into account the line mixing effect in the band profile calculation. This parameter depends on the perturbing gas type, and it is the same for all the bands of a molecule.

To adjust the C_b parameter for atmospheric applications, we chose the data obtained for N_2 mixtures. For CO_2 it was adjusted to the wing shape data beyond the band head of the ν_3 CO_2 band. The VC shape was then examined using the CO_2 spectra in the regions of ν_2, $\nu_2 + 2\nu_3$, $2\nu_2 - \nu_2$, $2\nu_1 - \nu_2$ bands. The agreement between the calculated and the measured shapes is quite satisfactory, including the temperature variation of absorption in the wing region. Similar studies were carried out for 3.6 μm band of O_3 in nitrogen.

The method was applied to the interpretation of atmospheric transparency data obtained in Shuttle experiments in the region of some CO_2 bands. The deviations of the measured data from those calculated as Lorentz line sums are explained with no empirical χ factors.

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H36

Ar-Broadening Coefficients in the ν_2 Band of HCN

Jean-Pierre BOUANICH [+], Ghislain BLANQUET[*],
and Jacques WALRAND[*]

[+] Laboratoire de Physique Moléculaire et Applications, CNRS, Université de Paris-Sud, Bâtiment 350, F-91405 Orsay cedex, France.
[*] Laboratoire de Spectroscopie Moléculaire, Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles, B-5000 Namur, Belgium.

Ar-broadening coefficients have been measured for 29 lines of HCN in the P, Q, and R branches of the ν_2 band, using a tunable diode-laser spectrometer (LS3-Lasers Analytics) in the spectral range 640 - 790 cm^{-1}. The collisional widths obtained by fitting Rautian profiles to the measured shape of the lines are significantly larger than those derived from Voigt profiles. The collisional broadenings have been performed on the basis of the Robert-Bonamy formalism with the atom-atom intermolecular potential. The calculated results in the P, Q, and R branches are in overall agreement with our experimental results and those of Pine[1] in the $\nu_1+\nu_2$ band, Varghese and Hanson[2] in the ν_1 band, and Lemaire[3] in the ν_2 band.

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H37

OBSERVATION OF A NON-THERMAL ORTHO-PARA RATIO OF H_3^+ IN HYDROGEN PLASMAS

D. Uy, M. Cordonnier*, R.M. Dickson, K.E. Kerr and T. Oka
Dept. of Chemistry and Dept. of Astronomy and Astrophysics, The
University of Chicago, Chicago, IL 60637, U.S.A.
*Laboratoire de Spectroscopie Hertzienne, Université des Sciences et
Technologies de Lille, 59655 Villeneuve d'Ascq, FRANCE

Although the extremely slow conversion between different nuclear spin modifications of molecules in radiative and collisional processes has been well-established, no observation of non-thermal ratios of spin modifications has been reported except for H_2 and its isotopic species. We have studied several transitions of H_3^+ using normal and para-H_2 as the source gases to see if we could detect a different ortho-to-para ratio of H_3^+. The reaction

$$H_2 + H_2^+ \rightarrow H_3^+ + H$$
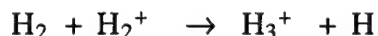
generates only para-H_3^+ if para-H_2 is used[1], and the subsequent proton hop reaction

$$H_3^+ + \tilde{H}_2 \rightarrow \tilde{H}_2H^+ + H_2$$
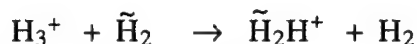
will retain para-H_3^+ while the hydrogen exchange reaction

$$H_3^+ + \tilde{H}_2 \rightarrow H_2\tilde{H}^+ + H\tilde{H}$$
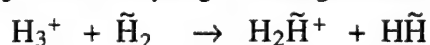
may convert para-H_3^+ to ortho-H_3^+. These and other reactions also convert para-H_2 to ortho-H_2 and so far it had been assumed that spin modifications are thermalized in plasmas.

We have detected a clear difference in the intensity ratios of the ortho and para H_3^+ lines, both in positive column and hollow cathode discharges, depending on whether normal or para-H_2 was used. This effect was more apparent for transitions originating from lower energy levels. The ion-neutral chemical kinetics, taking into account the spin modification, will be presented to analyze the observed results.

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H38

The Microwave Spectrum of the Open-Shell Complex NO-HF

C.R. Dennis, C.J. Whitham, B.J. Howard
The Physical and Theoretical Chemistry Laboratory,
South Parks Road, Oxford, OX1 3QZ, England

A detailed study of the complex NO-HF has been carried out using the technique of Fourier Transform Microwave Spectroscopy. There have been approximately a hundred hyperfine transitions recorded originating from the J=3/2(f)-1/2(f), J=3/2(e)-1/2(e) and J=5/2(e)-3/2(e) rotational levels.

A previous infrared study[1], provided the rotational constants which facilitated the search in the microwave region.

The hydrogen bond interaction is sufficiently strong to cause considerable quenching of the NO electronic orbital angular momentum giving rise to a Renner-Teller parameter ε_2 and a Zeeman interaction with the Earth's magnetic field. A magnetic interaction has been observed between the unpaired electron on NO and both the hydrogen and fluorine nuclei in the HF.

Initial analysis has shown that the Renner-Teller parameter ε_2 has a negative sign, indicating that the unpaired π^* electron is in the plane of the complex and an attractive interaction exists between NO and HF.

It is believed that this is the first such observation of a magnetic interaction induced by complexation. Such interactions are extremely sensitive to the nature of the forces between partners in a complex, and should be a common feature of microwave spectra of open-shell complexes involving magnetic nuclei such as hydrogen, nitrogen and fluorine.

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[1] W M Fawzy, G T Fraser, J T Hougen and A S Pine J. Chem. Phys. 93 (5) 2992

H39

THE CO:CO$_2$ COMPLEX IN SOLID ARGON

V. Raducu, D. Jasmin, P. Brosset, R. Dahoo, B. Gauthier-Roy

and L. Abouaf-Marguin

L. P. M. A. 4, place Jussieu 75252 Paris cédex 05

Inert matrices provide a suitable environment for the observation of weakly bound molecular complexes. The observed geometry is not necessarily the same as in a molecular beam, but the matrix technique allows the study of conformational changes, depending reversibly upon the temperature.

The vibrational spectrum of the CO:CO$_2$ complex is analysed in the CO region, and also in v_2 and v_3 regions of CO$_2$. In each region, two different features are found which are attributed to two different conformations of the complex on the basis of their temperature behavior. In the CO region, these two features appear on each side of the vibration of isolated CO (2138.49 cm^{-1}). A doublet is observed on the high frequency side (HF doublet, 2143.34 and 2143.01 cm^{-1}) at temperatures above 12 K. When cooling down to a lower temperature, this doublet partially converts into a narrow line (FWHM = 0.14 cm^{-1}) on the low frequency side (LF line, 2135.38 cm^{-1}), the total absorption remaining constant. The conversion process HF -> BF has been studied at different fixed temperatures between 5 and 9 K: at each temperature an equilibrium is reached, the equilibrium LF/HF ratio increasing when the temperature decreases. The conversion is slow (minutes) but fastens when the temperature increases. At 9 K the reverse process BF -> HF is faster (seconds).

Ab initio calculations of the total energy of an argon crystal doped with CO and CO$_2$ in adjacent sites have been performed at the " Laboratoire de Dynamique des Interactions Moléculaires". Two trapping conformations of slightly different stability have been found. In the more stable one CO and CO$_2$ are trapped in a T shaped geometry with the two C atoms contiguous: this configuration gives rise to the LF absorption. The observed change towards a high temperature "parallel" conformation is discussed on the basis of energy considerations.

H40

A HIGH RESOLUTION AND HIGH CONTRAST SPECTROMETER TO COMPETER WITH (FOURIER TRANSFORM) INTERFEROMETERS.

Patrick EVRARD and Jean-Louis STEHLE
SOPRA S.A., 26 Rue Pierre Joigneaux
F-92270 Bois-Colombes, France

Recently, a double monochromator, the model DMDP2000 has been successfully used in different fields of application : Raman, Brillouin and plasma kinetics spectroscopy. The instrument has been described in detail by V. MAZZACURATI and al in Ref.[1]. The most outstanding feature is the resolving power (10^6) to resolve Doppler shift and broadning, on a wide Spectral Range (from UV to NIR). The spectra taken with this dispersive optical spectrometer and with Fabry-Perot interferometers will be compared. The differences with the Fourier Transform interferometers due to line shape, contrast and temporal resolution, as well as luminosity (Ref.[2]) and finally, the ability of this spectrometer (coupled to a CCD matrix detector) to make spectral imagery will be presented.

1 - V. Mazzacurati, P. Benassi, G. Ruocco "*A new class of multiple dispersion grating spectrometers* - J. Phys. 21 (1988) 798 - 804.

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3 - W.G. Fastie "*Ebert spectrometer reflections*" - Phys. Today (Jan. 1991) 37 - 43.

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H41

High resolution wavenumber standards for the infrared.
(IUPAC Recommendations 1995)
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G. Guelachvili[1], M. Birk[2], Ch. J. Bordé[5], J. W. Brault[3], L. R. Brown[4], B. Carli[6], A. R. H. Cole[7], K. M. Evenson[8], A. Fayt[9], D. Hausamann[2], J. W. C. Johns[10], J. Kauppinen[11], Q. Kou[1], A. G. Maki[12], K. Narahari Rao[13], R. A. Toth[4], W. Urban[14], A. Valentin[15], J. Vergès[16], G. Wagner[2], M. H. Wappelhorst[14], J. S. Wells[8], B. P. Winnewisser[17], M. Winnewisser[17].
****

[1]Laboratoire de Physique Moléculaire et Applications, CNRS UPR-136, Université Paris-Sud, Bâtiment 350, 91405 ORSAY-cedex, France.

[2]Institute for Optoelectronic, DLR, D-82234 Wessling, Germany.

[3]NOAA Aeronomy Lab.R/E/AL5, 325 Broadway, Boulder, CO 80303, USA.

[4]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, 91109, USA.

[5]Laboratoire de Physique des Lasers, Université Paris-Nord, Avenue Jean-Baptiste Clément, 93430 Villetaneuse, France.

[6]Istituto di Ricerca sulle Onde Elettromagnetiche del CNR, Via Panciatichi 64, 50127 Firenze, Italy.

[7]School of Chemistry, The University of Western Australia, Nedlands, W.A. 6009, Australia.

[8]NIST, 524, 325 Broadway, Boulder, Colorado 80303, USA.

[9]Molecular Spectroscopy Laboratory, Catholic University of Louvain, Chemin du cyclotron, 2, B 1348 Louvain-la-Neuve, Belgique.

[10]Steacie Institute for Molecular Sciences, National Research Council, 100 Sussex Drive, Ottawa , Ont. K1A 0R6, Canada.

[11]University of Turku, Dept of Applied Physics, FIN-20500 Turku, Finland.

[12]Department of Chemistry, University of Washington, Seattle, Washington 98195, U.S.A.

[13]The Ohio State University, Department of Physics, 174 West, 18 th Avenue, Columbus, Ohio 43210-1106, USA.

[14]Institut für Angewandte Physik, der Universität Bonn, Wegelerstrasse 8, 53115 Bonn, Germany.

[15]Laboratoire de Physique Moléculaire et Applications, Tour 13, 3ème étage, Université P. et M. Curie et CNRS, 4 Place Jussieu, 75252 Paris-Cedex 05, France.

[16]Laboratoire Aimé Cotton, Bâtiment 505, 91405 Orsay-Cedex, France.

[17]Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, 35392 Giessen, Germany.
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The calibration of high resolution infrared spectra is generally more precise than accurate. This is the case even when they are recorded with Fourier transform interferometers. As a project for the Commission on Molecular Structure and Spectroscopy of IUPAC, the present note aims at improving the accuracy of wavenumber measurements in the infrared by recommending a selection of spectral lines as wavenumber standards for absolute calibration in the range from about 4 to about 7 000 cm^{-1}. Sources of frequency standards, on which the wavenumber determinations are based, are also given.

H42

DEVELOPMENT OF A HOLLOW CATHODE/RING-DOWN SPECTROMETER: CHARACTERIZATION OF CARBON CONTAINING SPECIES

Markus. Kotterer, Timothy. J. Slotterback and John. P. Maier
Institut für Physikalische Chemie, Universität Basel,
Klingelbergstr. 80, 4056 Basel, Switzerland

For the first time the novel technique of cavity ring-down spectroscopy (CRDS) has been combined with a Hollow Cathode (1 meter) discharge source. The combination of these two techinques provides a means by which non-fluorescing and long lived discharge species, normally undetectable in an combustion apparatus, can be probed. In the apparatus to be presented here pathlengths on the order of 10 km have been obtained. This has allowed molecular transitions to be readily observed at concentrations of 10^9 molecules/cm^3. Preliminary results for several ro-vibronic transitions of the C_2 and C_3 molecules will be presented.

H43

NEAR INFRARED SPECTROSCOPY AT 1.5 µm USING A HERRIOTT
MULTIPASS CELL

I.F. Howieson and G Duxbury[a],
N. Martin, T. Gardiner and P.T. Woods[b]

[a]Department of Physics and Applied Physics, University of Strathclyde,
John Anderson Building, 107 Rottenrow, Glasgow G4 0NG, Scotland.
[b]Division of Quantum Metrology, National Physical Laboratory,
Teddington, Middlesex

A multipass Herriott cell has been designed for use in near-infrared detection
and measurement of atmospheric trace gases. Using an astigmatic
arrangement path lengths of up to two hundred metres may be achieved in a
cell length of less than fifty centimetres.

A spectrometer based on this cell has been constructed and has exhibited a
sensitivity corresponding to an absorbance detection limit of better than one
part in 10^{-5}. A distributed feedback laser (DFB) operating at 1519 nm has
been used to detect nitrous oxide and ammonia, giving ppb detection for
these gases. In future a DFB laser near 1650 nm will be used to detect
methane with sub ppb sensitivity.

A breadboard version of the instrument is currently being assembled for
future field measurements in the lower stratosphere.

J1

OPTICAL STARK AND PPMODR STUDIES OF METAL CONTAINING MOLECULES

T.C. Steimle, A.J. Marr, M. Flores and B. Li

Dept. of Chemistry, Arizona State University

Tempe, AZ 85287-1604 U.S.A.

The combination of laser ablation/supersonic expansion molecular sources with laser induced fluorescence detection has greatly enhanced our ability to perform high resolution optical spectroscopy of transient metal containing molecules[1,2]. It has now become routine to record optical spectra of diatomic and small polyatomic metal radicals at the natural line width limit. In our laboratory these techniques have been incorporated into optical Stark and pump/probe microwave optical double resonance (PPMODR)[3] spectroscopic schemes. Optical Stark spectroscopy facilitates the determination of the permanent electric dipole moments, which is the most fundamental electrostatic property. PPMODR spectroscopy is a sensitive means of recording microwave and r.f. transitions for ground vibronic levels.

In this presentation a general review of these techniques will be given. Stark measurements for PtX (X=O,S,N, and C) and CaX (X=CCH, SH,NH$_2$) will be emphasized. A comparison with semi-empirical predictions[4] for the alkaline earth compounds will be made. PPMODR studies of CaSH, CaNC and PtS will be discussed.

1 -C. J. Whitham, B. Soep, J.-P. Visticot and A. Keller, J. Chem. Phys. 93, 991 (1990).

2 -B. Simard, A. J. James, and P.A. Hackett, J. Chem. Phys. 96, 2565 (1992).

3 -T.C. Steimle, D.A. Fletcher, K.Y. Jung and C.T. Scurlock, J. Chem. Phys. 97 2909, (1992).

4 -J. M. Mestdagh and J.-P. Visticot, Chem. Phys. 155, 79 (1991).

J2

MOLECULAR SPECTROSCOPY AND THE ACCURATE MEASUREMENT OF INTENSITIES USING FOURIER TRANSFORM INSTRUMENTS

J. Vander Auwera

Laboratoire de Chimie Physique Moléculaire C.P. 160/09
Université Libre de Bruxelles
50 avenue F. D. Roosevelt, 1050 Brussels, Belgium

Recent results obtained in the measurement of absorption line intensities using Fourier transform spectroscopy will be discussed. Two themes will be presented.

Infrared Fourier transform spectroscopy allows the measurement of very precise and accurate absorption line intensities. As a result, it is possible to observe and study qualitatively and quantitatively Herman-Wallis effects within vibrational bands as well as intensity borrowings between them induced by anharmonic and l-type resonances. In this context, regions of the infrared spectrum of OCS and the near infrared spectrum of N_2O have been studied. Results derived from absolute intensities for OCS and relative intensities for N_2O will be discussed.

The measurement of accurate absolute intensities is very important in the atmospheric context. However, many atmospheric species are unstable. As a result, the measurement of absolute intensities for such species faces the problem of the determination of their partial pressure in the equilibrium mixture required to produce it. For asymmetric rotors possessing a permanent electric dipole moment, it is possible to determine directly the partial pressure in the mixture by carrying out intensity measurements in the pure rotation spectrum observed in the far infrared. That technique and its application to absolute line intensity measurements in the v_2 band of HOCl, a temporary reservoir of chlorine atoms in the stratosphere, will be presented.

K1

Ab initio interpretation of the I.R. spectrum
of N_2O_4 in the region 300-600 cm^{-1}

Y. El Youssoufi*, J. Liévin* , B. P. Winnewisser**,
J. W. G. Seibert** and M. Herman*

* Laboratoire de Chimie Physique Moléculaire, Faculté des Sciences,
Cpi 160/09, Université Libre de Bruxelles, B-1050 Bruxelles, Belgium

**Physical Chemistry Institute, Justus Liebig University,
D-35392 Giessen, Germany

The infrared spectrum of N_2O_4 below 600 cm^{-1} was recorded at Giessen for three different resolutions and at temperatures from room temperature down to -60°C, at intervals of 10°C. For each temperature, spectra were recorded at a resolution giving a FWHM of 0.067 cm^{-1}, and 0.0067 cm^{-1}. At -40°C, a further spectrum with FWHM of 0.0023 cm^{-1} was recorded. The spectra with FHWM of 0.067 cm-1 emphasize the Q branch structure of the spectrum, and show a superposition of vibrational sequences, centered around 390, 420 and 550 cm^{-1}. The structure of the spectrum emerges most clearly at -60°C. The bands near 550 cm^{-1} have been analysed previously [1].

We present in this work a vibrational interpretation of the whole energy region by means of MP4/6-31G* *ab initio* calculations and of anharmonic normal coordinates variational calculations. The latter are based on 2-dimensional (Q4,Q6) and 3-dimensional (Q2,Q4,Q7) effective potential energy and dipole moment surfaces. The geometrical relaxation along the torsional motion is taken into account in these calculations. The theoretical spectrum (energies and intensities) matches well with the experimental one and an unambiguous assignment is proposed.

[1] J. Koput, J.W.G. Seibert and B.P. Winnewisser, Chem. Phys. Lett. 204, 183 (1993).

K2

FOURIER TRANSFORM SPECTROSCOPY AND PHOTOASSOCIATION SPECTROSCOPY OF COLD ATOMS: THE Rb$_2$ $^1\Pi_g$ AND 0^-_g ELECTRONIC STATES POTENTIAL ENERGY CURVES UP TO 100 Å

C.Amiot
Laboratoire Aimé Cotton, C.N.R.S. II, Bât. 505, Campus d'Orsay, 91405
Orsay France

The Rb$_2$ 1g state, correlating to the $5\,^2S_{1/2} + 5\,^2P_{3/2}$ dissociation limit, was recently observed, within 35 cm^{-1} of the limit, by Cline et al [1] using cold-atom photoassociation spectroscopy (P.A.S.).

Also, the full potentialities of P.A.S. were demonstrated by the observation of the 0^-_g pure long-range state [1]. Combining our previous results on the $^1\Pi_g$ state (correlating to 1g at large internuclear distance), observed up to 16 Å, and obtained by high resolution Fourier spectroscopy [2,3] with cold-atoms data, it has been possible :

    1- to assign vibrationnally the 1g spectrum recorded by P.A.S.;

    2- to construct realistical potential energy curves for the 1g and 0^-_g states, extending up to 100 Å;

    3- to derive the long-range C$_3$ parameter for both states and to compare it with the most recent previsions [4].

    The figure below depicts the two potential curves up to 100 Å (the insert shows the structure of the long-range 0^-_g potential curve).
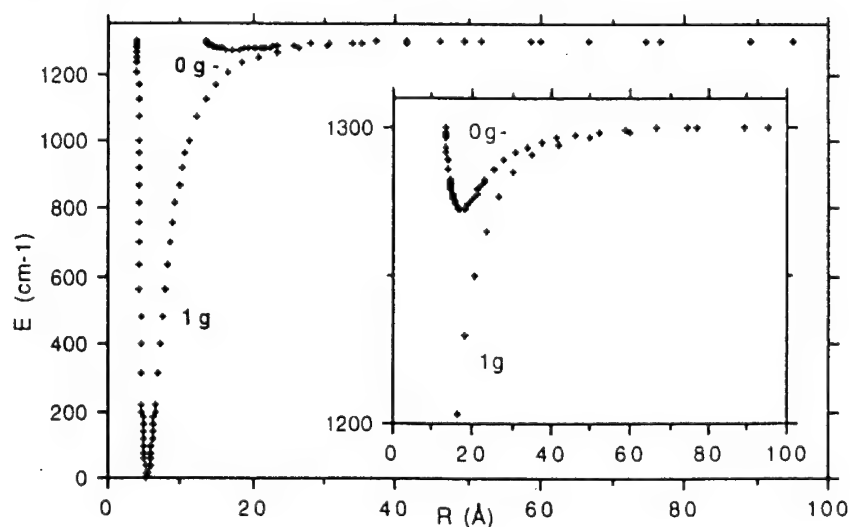
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[2] C. Amiot, Mol. Phys. 58, 667 (1986).
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K3

DUNHAM SERIES COEFFICIENTS UP TO 20-TH ORDER

M. Rytel and T. Rytel
Atomic and Molecular Physics Laboratory, Pedagogical University
PL-35310 RZESZÓW, Rejtana 16A, Poland

The method for obtaining Dunham series coefficients based on the combination of the hypervirial theorem[1,2,3] and the Hellmann-Feynman theorem[2,4,5] was used. The very efficient procedure is analogous to the one used by Swenson and Danforth for the simple x^{2N} potential.[6] A very similar method was proposed by Fernandez and Ogilvie.[7]

The algorithm has been programmed in the MAPLEV R3. Expressions for Dunham Y_{lk} coefficients are obtained obtained for terms up to the order of 20. They have enabled us to extend remarkably the number of the exact interrelations for the mass-independent parameters U_{lk} published formerly by Tyuterev and Velichko.[8]

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[2] - F. M. Fernandez and E. A. Castro, in „Lecture Notes in Chemistry", Vol. 43, Springer Verlag, Berlin, 1987.

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K4

SPIN-ORBIT SPLITTINGS IN CALCIUM MONOHALIDES.
A RELATIVISTIC LIGAND FIELD APPROACH

Mohammed BENCHEIKH

Laboratoire de Dynamique Moléculaire et Photonique,

URA CNRS n° 779

U.S.T de Lille, UFR de Physique, Bât. P5

59655 Villeneuve d'Ascq Cedex - FRANCE

To handle the relativistic effects in chemical physics, they are usually evaluated by the first order perturbational approach using non-relativistic wave functions. Among the most important relativistic effects, only the spin-orbit effect is of spectroscopic interest because it splits the degenerate configurations.

In the framework of the closed shell ligand-ligand field theory (CSLLFT), all the calculations carried out up to now have treated the spin-orbit doubling by the perturbational approach. The diagonal and non-diagonal atomic spin-orbit parameters, respectively ζ_{nl} and $\zeta_{nn'l}$ of the alkaline earth ion have been used as input data. The formers are evaluated from the observed spin-orbit splittings in the free ion via Lande rule, while the latters are estimated semi-empirically. The most justified rule has been stated by Jakubek and Field (J. Chem. Phys. **98**, 6574 (1993)) :

$$\zeta_{nn'l} = \left(\zeta_{nl}\,\zeta_{n'l}\right)^{1/2}$$

assuming a phase convention based on *ab initio* calculations on CaF.

This work aims to calculate the spin-orbit splittings of the $A^2\Pi$, $B'^2\Delta$ and $C^2\Pi$ electronic states of Calcium monohalides using a relativistic formulation of the CSLLFT (RLFT) in order to make the theory free of the non-diagonal spin-orbit parameters $\zeta_{nn'l}$.

K5

REMPI SPECTROSCOPY OF THE $E^1\Pi$ AND $C^1\Sigma^+$, v=0 AND v=1 STATES OF $^{12}C^{16}O$ AND $^{13}C^{16}O$ ACCIDENTAL PREDISSOCIATION PHENOMENA

Patrice CACCIANI*, Wim HOGERVORST and Wim UBACHS

Laser Centre Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam,

the Netherlands

*Permanent address: Laboratoire Aimé Cotton, Bat 505 Campus d'Orsay,

91405 Orsay cedex, France

The $E^1\Pi$, v=0 and v=1 levels of CO are excited from the ground state by one VUV- and two- UV photon transitions, probing e and f Λ-doublet states[1] New accidental predissociations were found in the $E^1\Pi$, v=0 state for high J values (J_e=31, 41, 44 for $^{12}C^{16}O$ and J_e=41, 50 for $^{13}C^{16}O$).

The predissociation phenomenon of $E^1\Pi$, v=1 around J=7 was reinvestigated and found to be perturbed by all three spin-components of a $k^3\Pi$, v=5 state. Measurements of spectral line shifts were modeled assuming a spin-orbit coupling between $E^1\Pi$ and the $^3\Pi_1$ component of the $k^3\Pi$ state. Relative predissociation lifetimes of $k^3\Pi$, v=3, 4 and 5 with respect to $E^1\Pi$, v=0 and v=1 are deduced from an analysis of observed intensity effects.

The $C^1\Sigma^+$ - $X^1\Sigma^+$ (1,0) and (0,0) bands have been also investigated by the same two methods. First the method of 2+1 resonance enhanced ionization yielded information on highly excited rotational states up to J≈50, while the second method of 1 VUV + 1 UV photoionization provided highly accurate calibrations.

The $E^1\Pi$, v=1 state and $C^1\Sigma^+$ v=1 of $^{12}C^{17}O$ are observed for the first time.

Molecular constants for $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{17}O$ are derived.

[1] P. Cacciani, W.Hogervorst and W. Ubachs accepted in J. Chem. Phys.

K6

THEORETICAL STUDY OF THE ELECTRONIC STRUCTURE OF BaK

N. Boutassetta, A.R. Allouche and M. Aubert-Frécon

Laboratoire de Spectrométrie Ionique et Moléculaire, CNRS et Université
Lyon I, Campus de la Doua, Bât. 205, F69622 Villeurbanne Cedex, France.

A theoretical study of the structure of all the molecular states dissociating into the six lowest limits has been performed for the molecule BaK as yet unobserved nor investigated theoretically. Our aim is that such predictions should be useful for further observations, as they were for our previous investigations of BaLi[1]. The method used is basically the same as that we previously used for BaLi and for BaNa[2]. The Ba atom is treated through a relativistic non-empirical effective ten-electron core-potential while K is described by a one-electron core-potential. Molecular orbitals are obtained from a SCF calculation and a CI calculation is performed for the three active electrons using the CIPSI algorithm. Core-polarization potentials are introduced in order to take some account of the core polarization effects and of the core-valence correlation. Spin-orbit effects are evaluated through a semi-empirical spin-orbit pseudopotential for barium (they have been neglected for K) by use of the CIPSO algorithm.

Potential energy curves and spectroscopic constants for bound states will be presented.

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[2]-N. Boutassetta, A.R. Allouche and M. Aubert-Frécon, Chem. Phys. 189, 33(94)

K7

Investigation of the $e^6\Pi$ - $a^6\Delta$ Transition in the Green System of FeH at 532nm.

D. M. Goodridge, R. T. Carter, and J. M. Brown

The Physical and Theoretical Chemistry Laboratory,

South Parks Road, Oxford, OX1 3QZ.

The green system of FeH, previously observed by Carroll *et al*[1], has been studied using the technique of laser excitation spectroscopy[2]. The spectrum was recorded at Doppler resolution, using a sample produced by the gas phase reaction between H atoms and $Fe(CO)_5$, at ambient temperatures. The transition has been assigned as $e^6\Pi$ - $a^6\Delta$; both states exhibiting significant perturbation. Dispersed fluorescence studies, together with term values and the vibrational intervals of the three lowest spin components of the $a^6\Delta$ state[3], aided assignment of many of the observed lines to the $\Omega=3/2$ - $\Omega=5/2$, $\Omega=5/2$ - $\Omega=7/2$, and $\Omega=7/2$ - $\Omega=9/2$ subbands. Accurate term values have been determined for the $e^6\Pi$ state.

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[3] R. T. Carter and J. M. Brown, J. Chem. Phys. **101**, 2699 (1994).

K8

FAST ION BEAM LASER SPECTROSCOPY OF $^{13}CO_2^+$: LASER INDUCED FLUORESCENCE OF THE $\tilde{A}^2\Pi_u$ - $\tilde{X}^2\Pi_g$ ELECTRONIC TRANSITION[1].

M. Larzillière, A.Roney and N. Varfalvy

Laboratoire de physique atomique et moléculaire

Département de physique, Université Laval

Québec Canada G1K 7P4.

Laser induced fluorescence of a fast ion beam has been applied to the $^{13}CO_2^+$ (0,0,0) $\tilde{A}^2\Pi_u$ - (0,0,0) $\tilde{X}^2\Pi_g$ UV electronic transition. The high resolution (0.005 cm^{-1}) of the F.I.B.LA.S. method allows us to evaluate the isotopic shift, to appreciate the contribution of the central atom when determining molecular parameters and, for the first time, to determine the influence of the central atom on hyperfine structure. Absolute calibration of the $^{13}CO_2^+$ spectra is obtained by means of a $^{12}CO_2^+ - {}^{13}CO_2^+$ spectrum, allowing calibration via F.T. spectra of $^{12}CO_2^+$ [2].

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[1]Submitted to J. Mol. Spect.

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K9

$S_1 \longleftarrow S_0$ SPECTROSCOPY AND S_1 DYNAMICS OF 4- AND 5-METHYLPYRIMIDINE

H. Bitto and S. Gfeller

Physikalisch-Chemisches Institut der Universität Zürich,

Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

The $S_1(\pi^*) \longleftarrow S_0(n)$ spectroscopy and S_1 dynamics of 4- and 5-methylpyrimidine were studied under collisionless conditions in a supersonic jet using time-resolved spectroscopy with near Fourier transform-limited nanosecond laser pulses. The bandwidth of about 200 MHz allowed us to resolve single rovibronic transitions and, therefore, to study the effects of rotation and internal rotation on the dynamics. Futhermore, the two isomers having different symmetry provide an example of the effect of symmetry.

We investigated vibronic bands with an excess energy of up to 1000 cm^{-1}. For both isomers all transitions accessing the ground state of methyl internal rotation $(0a_1)$ show c-type rotational structure of a prolate asymmetric top.

The dynamics of individual rovibronic S_1 levels is governed by spin-orbit interaction to quasi-isoenergetic rovibronic T_1 levels. Coherent excitation of the resulting eigenstates leads to fluorescence decays with superimposed quantum beats and to biexponential decays. The density of coupled triplet states inferred from the biexponential decays increases with rotational quantum number J of the excited rovibronic level and with excess energy. Symmetry restrictions reduce the density in the isomer (5-methylpyrimidine) of higher symmetry (C_{2v}) to one half of that in the isomer of C_s symmetry at the same excess energy. The rotational state dependence of the lifetimes makes possible an estimate of the lifetimes of the zero-order states. We found no dependence of the dynamics on internal rotation.

K 10

NEW REFINED POTENTIAL ENERGY SURFACES FOR H$_2$O AND H$_2$S

OLEG L. POLYANSKY

Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany.

PER JENSEN

FB 9 – Theoretische Chemie, Bergische Universität – Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany.

JONATHAN TENNYSON

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom.

The potential energy surfaces for water and hydrogen sulfide have been refined by fitting to experimental data. The calculations were carried out by means of the technique described previously[1], which combines MORBID calculations with calculations involving an exact kinetic energy operator. The potential energy expansion of Ref. 1 was extended with terms of higher order in the vibrational coordinates, and this made it possible to reduce the discrepancy for the highest vibrational states of water from about 100 cm^{-1} to less than 1 cm^{-1}. The input data for the water fitting comprised 3500 energy levels (out of about 4000 known experimentally) with $J \leq 14$ and $K_a \leq 14$. A standard deviation of 0.35 cm^{-1} was obtained. We express the dependence of the potential energy function on the bending angle as a cosine expansion, and we demonstrate that with this expansion, we can make reliable extrapolations of the bending energies to higher v_2 values.

For H$_2$S, we have extended the input data used in previous MORBID fittings[2] by the energies of 13 newly measured vibrational states with $v_2 \leq 5$. Further, we have included the rotational term values in the ground vibrational state and the ν_2 state for $J \leq 14$. A standard deviation of 0.22 cm^{-1} for the vibrational band origins was obtained in the framework of exact kinetic energy Hamiltonian.

We believe that in order to improve the potential energy surfaces obtained in the present work, it will be necessary to consider explicitly the nonadiabatic corrections to the kinetic energy operator resulting from the breakdown of the Born-Oppenheimer approximation. We will present numerical calculations supporting this conclusion.

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K11

HIGH RESOLUTION FOURIER TRANSFORM AND DIODE LASER SPECTRA OF THE 1940 cm⁻¹ BAND SYSTEM OF COF_2 AT STRATOSPHERIC TEMPERATURES.

Geoffrey Duxbury, Mark McPhail and Robert McPheat

Department of Physics and Applied Physics, University of Strathclyde, John Anderson Building, 107 Rottenrow, Glasgow G4 0NG, Scotland.

The absorption coefficients of the P and R branch transitions of the ν_1 band of COF_2 at 1943 cm⁻¹, which are used for stratospheric retrievals by Rinsland and his colleagues, have been measured both at room temperature, and at 197 K, at a resolution of 0.005 cm⁻¹. The carbonyl fluoride was contained in a cell cooled by passing dry nitrogen through a liquid nitrogen trap, and was housed within the fore optics box of a Bomem Fourier transform spectrometer.

To allow a more complete rotational analysis, high resolution diode laser spectra of portions of the R branch have also been recorded at Doppler limited resolution using a lead salt diode laser maintained at ca. 12 K by a closed cycle liquid helium cooler. Wavelength control was possible by ramping over individual longitudinal modes, and a cold head vibration limitation system has recently been added. From these data an improved calculation of synthetic absorption spectra has been carried out, and arotational analysis is in progress in which Fermi and Coriolis resonances are included.

K12

ACCOUNTING FOR THE ANOMALOUS CENTRIFUGAL DISTORTION IN THE HDO MOLECULE

L. H. Coudert

**Laboratoire de Physique Moléculaire et Applications
Unité Propre du C.N.R.S., Université Pierre et Marie Curie
Tour 13 - Case Courrier 76 - 4 Place Jussieu
F-75252 Paris Cedex 05, France**

Although in the HDO molecule centrifugal distortion effects are not as strong as in the water molecule,[1] the HDO molecule is nontheless a good candidate for testing theoretical models designed to account for the anomalous centrifugal distortion. In addition to that, this molecule will also give us the opportunity for studying these effects in a triatomic molecule having no two-fold axis of symmetry.

In this paper, a new treatment aimed at the calculation of the rotational energy of the HDO molecule and accounting for the anomalous centrifugal distortion will be presented. This approach, based on the one developed for the water molecule,[2] involves deriving a zeroth-order Hamiltonian, written with the help of Radau's coordinates, in which the large amplitude bending ν_2 mode as well as the overall rotation of the molecule are treated simultaneously. However, in the present case, due to the lack of two-fold axis of symmetry, this zeroth-order Hamiltonian contains a term arising from a non-diagonal component of the inertia tensor as well as a term describing the Coriolis-coupling between the large amplitude bending mode and the rotation of the molecule. This new treatment is used to perform an analysis of the infrared[1] and microwave[3] data of the molecule. It allows us to account for the latter set of data with an R.M.S. deviation of 0.15 MHz, while a value of 2.26 MHz was obtained with a conventional Watson-type Hamiltonian.[1] Information on the potential energy function is also obtained.

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K13

HIGH-ORDER DERIVATIVES OF THE DIPOLE MOMENT FUNCTION FOR THE OZONE MOLECULE

O. Sulakshina, Vl G. Tyuterev, A. Barbe

G.S.M.A., U.A. CNRS D 1434

Faculté des Sciences

BP 347 - 51062 REIMS Cédex - France

Through the fit of experimental intensities the transition moment coefficients of all the cold bands with $\Delta V = 3$ except $3v_2$ and also for the difference band $v_1+v_3-v_2$ have been obtained. We have used all these data to determine the third derivatives of dipole moment function.

The theoretical formulae for XY_2 are given in a suitable form permitting to use recurrent procedure.

The problem of the sign of transitions moment constants is partly solved using higher order terms in the expansion of the transition moment operators as it was done previously for the first derivatives [1].

[1] - J.M. Flaud, C. Camy-Peyret, C.P. Rinsland, M.A M. Smith, V. Malathy Devi, Atlas of Ozone spectral parameters from microwave to medium infrared, Academic Press, 1990.

K14

H$_2$Te : HIGH RESOLUTION STUDY OF THE ν_1, ν_3 AND $\nu_1 + \nu_2$, $\nu_2 + \nu_3$ BANDS

J.-M. Flaud, Ph. Arcas, M. Betrencourt

Laboratoire de Physique Moléculaire et Applications

Unité propre du CNRS, associée aux Universités Paris VI et Paris XI

Bat. 350, Université Paris XI, 91405 Orsay Cedex, France

H. Bürger and O. Polanz

Anorganische Chemie, FB9, Universität-Gesamthoschshule,

42097 Wuppertal, Germany

Using high resolution (0.003 cm^{-1}) Fourier transform spectra of natural hydrogen telluride recorded in the 5- and 3.3 µm regions, an extensive analysis of the ν_1, ν_3, $\nu_1 + \nu_2$ and $\nu_2 + \nu_3$ bands of the six isotopic variants ^{130}Te, ^{128}Te, ^{126}Te, ^{125}Te, ^{124}Te, ^{123}Te and ^{122}Te has been performed. The upper states rotational energy levels were derived by adding to the ground state levels (calculated using recent constants, P. Jensen and P. Kozin, private communication) the observed transitions. These experimental energy levels were then least squares fit using an Hamiltonian model which takes explicitly into account the strong Coriolis interaction between the vibrational states $\left(v_1\, v_2\, v_3\right)$ and $\left(v_1 - 1\, v_2\, v_3 + 1\right)$. In this way all the experimental levels of {(100), (001)} and {(110), (011)} were calculated to within the experimental uncertainties and a precise set of vibrational energies, and rotational and coupling constants was derived for each isotopic variant.

K15

OBSERVATION AND CALIBRATION OF NIR LINES OF WATER USING A DIODE LASER SPECTROMETER

T D Bevis, J G Baker and N J Bowring
Department of Physics and Astronomy,
University of Manchester, M13 9PL, UK

We have previously reported on the construction of a thermally scanned and frequency locked nir gas spectrometer using commercial laser diodes in the 788-790 nm region.[1,2] By designing a cooling system which makes use of a range of diodes and functions over the range 0-35°C, by enhancing the precision and resolution of the computerised temperature control system, and by introducing a 'crossfire' frequency measurement technique employing a Michelson wavemeter and two separate precision Fabry-Perot interferometerss, we have been able to count interference fringes over mode hops and measure spectral frequencies in the range 775-790 nm reproducibly to 0.003 cm^{-1} accuracy.

We demonstrate the use of an on-line spectral convolution computer program which has enabled us to detect and locate specral lines of water of reported intensities[3] as low as 10^{-27} mols $\text{atm}^{-1}\text{cm}^{-2}$, and give a comparative listing of observed spectral lines which include several not previously reported[3,4]. It is suggested that development of instruments of this kind may prove useful in providing nir wavelength standards.

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K16

STUDIES ON THE INFRARED SPECTRUM OF H_2S

O.N. Ulenikov, A.B. Malikova, G.A. Onopenko

Tomsk State University, Tomsk, 634050, RUSSIA

S. Alanko, M. Koivusaari, and R. Anttila

Department of Physical Sciences, University of Oulu, FINLAND

The high resolution spectrum of H_2S in natural isotopic abundance has been measured within two regions by using the Fourier transform spectrometer Bruker IFS 120 HR in Oulu. The first range from 840 to 1360 cm^{-1} covers the unperturbed bending fundamental band ν_2 (1182 cm^{-1}). The most prominent features in the spectrum are due to $H_2^{32}S$ (95 per cent of the molecules). We assigned 726 lines of this species with $J_{max} = 17$. From the observed lines 226 upper state energy levels could be derived. They could be fitted with a standard deviation of 9.9×10^{-5} cm^{-1}. For $H_2^{34}S$ 126 energy levels were evaluated and they could be fitted with almost the same accuracy as above. For the less abundant species $H_2^{33}S$ 57 weak lines were assigned.

The other region studied, 3300- 4080 cm^{-1}, covers the combinations of ν_2 with the S-H stretching modes ν_1 and ν_3 and also the second overtone $3\nu_2$ of the bending mode. As $3\nu_2$ is very weak, it needed a measurement of its own by using a path length of 67 m and a pressure of 400 Pa. There is a very strong Coriolis resonance between $\nu_1+\nu_2$ (3779 cm^{-1}) and $\nu_2+\nu_3$ (3789 cm^{-1}). In addition it was necessary to include in the model the Coriolis interaction $\nu_2+\nu_3/3\nu_2$ and the Fermi resonance $\nu_1+\nu_2/3\nu_2$. In this region 1948 lines were assigned. The highest J values were 18, 14 and 10 for $H_2^{32}S$, $H_2^{34}S$, and $H_2^{33}S$, respectively. The model explained the energy levels calculated from the observed line positions so that the standard deviations in the fits were 1.3×10^{-4} cm^{-1} for $H_2^{32}S$ and somewhat worse for other two species. Hot band lines of $H_2^{32}S$ were also observed in both the regions.

K17

EFFECTIVE HAMILTONIAN FOR INVERSION-ROTATION STATES OF AMMONIA-LIKE MOLECULES.

K.Sarka

Faculty of Pharmacy, Comenius University, Odbojárov 10,

832 32 Bratislava, Slovakia

and H.W. Schrötter

Sektion Physik der LMU München, Schellingstr. 4,

D-80799 München, Germany

A new reduction scheme satisfying all symmetry requirements has been applied. Result of the reduction is effective correlation-free Hamiltonian describing inversion-rotation states of ammonia-like molecules. Discrepancies between existing theories and actual fitting schemes applied to experimental data are explained. The results are compared with the data from the literature.

K18

HIGH RESOLUTION INFRARED STUDY OF THE MID-IR AND CH-STRETCHING REGIONS OF $H_2C={}^{13}C=CH_2$

F. Hegelund[a], O. Polanz[b] and H. Bürger[b]

[a] Department of Chemistry, Aarhus University

DK-8000 Aarhus C, Denmark.

[b] FB-9, Universität-GH

D-42097 Wuppertal, Germany.

High resolution Fourier transform spectra of the isotopic species $H_2C={}^{13}C=CH_2$ have been recorded of the $\nu_7(B_2)$, $\nu_9+\nu_{11}(B_2)$, $2\nu_{10}(B_2)$, $\nu_6(B_2)$, $\nu_5(B_2)$ and $\nu_8(E)$ bands on the Bruker 120 HR FTIR spectrometer in Wuppertal.

Local perturbations are discussed on the basis of single subband analysis of the bands. A detailed analysis of the $\nu_7/\nu_9+\nu_{11}$ band system in the 1300-1400 cm^{-1} region is presented, taking into account the strong Fermi resonance between ν_7 and $\nu_9^1+\nu_{11}^1$, weaker higher order anharmonic resonances with the $4\nu_{11}^2$ level, and rotational ℓ-type resonances within $\nu_9+\nu_{11}$. The $2\nu_{10}^2$ band at 1687 cm^{-1} is analyzed by using a model including local (x,y)-Coriolis perturbations with $\nu_4+\nu_{10}$ and $\nu_7+\nu_{11}$, and rotational ℓ-type resonances within $2\nu_{10}$. Spectroscopic constants for the bands, various interaction constants, and band center values for the perturbers are presented.

Band centers for all the IR-active fundamentals of $H_2C={}^{13}C=CH_2$ have been obtained, and ^{13}C-wavenumber shifts relative to normal allene are given.

K19

High-resolution FTIR study of the $\nu_2+\nu_4$ and $\nu_4+\nu_5$
rovibrational bands of $CH_3^{79}Br$ between 4200 and 4600 cm^{-1}.

N.BEN SARI-ZIZI,Laboratoire de Spectronomie physique appliquée,
Faculté des Sciences,Université Mohammed V,B.P.1014,RABAT(Agdal)
Morocco.
C.ALAMICHEL,Laboratoire de Photopysique moléculaire du CNRS,
Bâtiment 213,Université Paris-Sud,91405 ORSAY,France.

The $\nu_2+\nu_4$ and $\nu_4+\nu_5$ bands of $CH_3^{79}Br$ have already
been studied by di Lauro and Velino (1) who assigned 1356 lines
and obtained a r.m.s. deviation of 0.037 cm^{-1}, using a sample of
natural bromide and a BOMEM interferometer at a resolution of
about 0.015 cm^{-1}.

Using a better spectrum (resolution of about 0.006 cm^{-1})
recorded by G.GUELACHVILI on his FTIR interferometer with a sample
of pure $CH_3^{79}Br$ provided by H.Bürger, we assigned more than 4600
lines of the $\nu_2+\nu_4$ and $\nu_4+\nu_5$E bands, despite overlaps with
$3\nu_5^{\pm1}$, $\nu_1+\nu_5$ and $\nu_3+\nu_4+\nu_6$E. No lines of the parallel component of
$\nu_4+\nu_5$ have been observed,although its existence is unquestionable
because of its effects on the $\nu_2+\nu_4$ band. A least squares fit,
taking into account the x-y Coriolis resonance between the upper
levels of $\nu_2+\nu_4$ and of both components of $\nu_4+\nu_5$, the $\ell(2,2)$
resonance inside the ν_4 mode and also two localized interactions
(an anharmonic resonance between the K=2 upper levels of $\nu_4^1+\nu_5^1$
and $2\nu_2+2\nu_6^2$, and a Coriolis resonance between the K=8 upper
level of $\nu_2+\nu_4^{-1}$ and the K=9 upper level of $\nu_1+\nu_2$), gave a r.m.s.
deviation of 0.029 cm^{-1} over 4180 lines. Several other local
perturbations have been observed, but, because of the lack of
information and the high number of quanta involved in the possible
perturbers, it has not been possible to incorporate them in the
general model. The local interaction between $\nu_2+\nu_4$ and $\nu_1+\nu_2$
allowed us to determine the experimental band centre of $\nu_1+\nu_2$.

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Diode-Laser Spectroscopy: Absolute Line Intensities of ν_3 Band of $^{12}CH_3F$ at 9.6 μm

Muriel LEPERE, Ghislain BLANQUET and Jacques WALRAND

Laboratoire de Spectroscopie Moléculaire, Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles B-5000 Namur (Belgium)

Methyl fluoride, one of the minor molecular constituents of Venus atmosphere, is a symmetric top of C_{3v} symmetry. Using the equivalent width measurement method, we have determined the strengths of individual lines in the P and R branches of ν_3 band of methyl fluoride. The accurate determination of the absolute wave number of the lines was made from spectral constants given by Papousek[1] [2].

The purity of our sample was 99.0 %. The absorption path length was set between 0.1138 and 8.17 m. The spectral range (994.9 to 1093.8 cm^{-1}) was covered with two Pb-Sn-Te diodes. Spectra were recorded under a pressure ranging from 0.1 to 1.0 mbar, at room temperature and finally normalised to T = 296 K. The relative calibration was performed using a confocal etalon with a fringe spacing of 0.0097711 cm^{-1}. For a given transition under study, four records were made at different pressures, from which we deduced an average value of the line intensity.

So we obtained a set of about ninety such averages corresponding to $3 \leq J \leq 34$ and $3 \leq K \leq 15$. From these data, we have determined by least squares fitting the vibrational band strength S_V^0 at 297 K. The first Herman-Wallis coeficient we determined is very small.

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[2] D. Papousek, Yen-Chu Hsu, Hann-Sen Chen, P. Pracna, S. Klee, M. Winnewisser, J. Mol. Spectrosc. **159**, 33-41 (1993)

K21

FORCE FIELD AND DIPOLE MOMENT DERIVATIVES OF METHANE

A.MOURBAT AND M.LÖETE

LABORATOIRE DE PHYSIQUE DE L'UNIVERSITE DE BOURGOGNE

URA CNRS 1796, FACULTE DES SCIENCES,

6,boulevard Gabriel, 21000 Dijon, France

The symmetry force constants and Dipole moment derivatives of methane have been refined simultaneously using 157 " observed " parameters obtained from analyses of energy levels,line strengths or Stark spectra of the tetrahedral species $^{12}CH_4$,$^{13}CH_4$,$^{12}CD_4$ and$^{13}CD_4$.

The 13 cubic constants and 21 quartic constants of the potential function have been determined in addition to the 7 second-order and 5 third-order constants of the dipole moment function.The " observed " parameters have been reproduced with a standard deviation of 4%.

Some parameters of the Hamiltonian and of the dipole moment can be then predicted.

K22

Determination of Induced Dipole Moments in the ν_2/ν_4 Dyad of SnH$_4$ by Linear Stark Effect

M. LÖETE AND M.P. COQUARD
Laboratoire de Physique de L'Université de Bourgogne,
URA CNRS 1796, Faculté des Sciences,
6 Bd Gabriel, 21000 Dijon, France

Y. OHSHIMA, AND M. TAKAMI
The Institute of Physical and Chemical Research (RIKEN),
Wako, Saitama 351-01, Japan

Applying the Doppler-free infrared infrared double resonance technique, the linear Stark splitting of several rotational E−symmetry energy levels has been observed in the ν_2/ν_4 dyad of SnH$_4$. A signal appears when two transitions sharing a common level are excited resonantly with two coherent radiations. If the ir transitions obey the perpendicular selection rule $\Delta M = \pm 1$, the Stark levels with $\Delta M = \pm 2$ are coupled in the upper or the lower states, allowing thus direct measurements of the splitting.

In order to describe the linear Stark effect, we have used a Stark Hamiltonian matrix which reduces in case of weak electric fields to a 2×2 matrix model. Its off-diagonal element is directly the linear Stark splitting of an E−level and is proportional to the M quantum number, to the electric field and to an effective dipole moment. The latter is expressed in terms of Stark coefficients, affected each by an induced dipole moment parameter.

¿From the measurements and from the calculation of the Stark coefficients, these induced dipole moment parameters have been determined to be $\mu_0 = 1.499(11) \times 10^{-5}D$ (centrifugal distorsion-induced dipole moment), $\mu_{44} = -1.317(42) \times 10^{-2}D$ (dipole moment induced by the ν_4 vibration, first order approximation) and $\mu_{24} = 3.94(23) \times 10^{-2}D$ (vibration-induced dipole moment between the $v_2 = 1$ and the $v_4 = 1$ states).

K23

HOT BANDS IN THE REGION OF THE BENDING
VIBRATIONS ν_4 AND ν_5 OF HCCI

Anne - Maaria Tolonen

Department of Physical Sciences, University of Oulu

Linnanmaa, 90570 Oulu, Finland

The high resolution infrared study concerning the fundamental bands
of the HCCI molecule has recently been completed in our laboratory[1].
Later, the detailed analysis of the hot bands in the region of the ν_5
bending fundamental was published[2]. The series of these studies has
now been continued. One aim of the present work was to determine
the rovibrational constants characterizing the CCH bending (ν_4) of the
molecule. This goal was achieved by analysing the hot bands $2\nu_4^{0,2} \leftarrow \nu_4^1$
at 615.33 cm^{-1} ($\Sigma \leftarrow \Pi$) and at 635.74 cm^{-1} ($\Delta \leftarrow \Pi$), together with
the results of the ν_4 fundamental[1].

The second object was to study the combination level $v_4 = v_5 = 1$. For
this purpose both the hot bands $(\nu_4 + \nu_5)^{0,2} - \nu_5^1$ and $(\nu_4 + \nu_5)^{0,2} - \nu_4^1$
were used. The hot bands in the ν_4 region are fairly strong and they are
found at 627.85 cm^{-1} ($\Sigma^- \leftarrow \Pi$), 630.77 cm^{-1} ($\Sigma^+ \leftarrow \Pi$), and 630.14
cm^{-1} ($\Delta \leftarrow \Pi$). In the ν_5 region the weak hot bands $(\nu_4 + \nu_5)^{0,2} - \nu_4^1$
were observed at 259.08 cm^{-1} ($\Sigma^- \leftarrow \Pi$), 262.00 cm^{-1} ($\Sigma^+ \leftarrow \Pi$), and
262.41 cm^{-1} ($\Delta \leftarrow \Pi$).

The spectrum of the ν_4 region was measured with the Bruker IFS 120 HR
Fourier spectrometer in Oulu with the instrumental resolution of 0.0014
cm^{-1} leading to the experimental linewidth of 0.0025 cm^{-1}, whereas the
ν_5 spectrum was recorded in Lund, Sweden, also with a Bruker IFS 120
HR. The experimental linewidth in the ν_5 spectrum was 0.0010 cm^{-1}.
The details of the measurements and the results of the analyses will be
discussed.

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K24

Vibrational Analysis of the Infrared Spectra of ClONO$_2$ and
BrONO$_2$: Harmonic Force Fields of the Halogen Nitrates

J. ORPHAL[†], M. MORILLON-CHAPEY[‡], AND G. GUELACHVILI[‡]

[†] *Institute of Environmental Physics, University of Bremen, P.O. Box 330440,
28334 Bremen, Germany, e-mail: orphal@gome1.physik.uni-bremen.de*
[‡] *Laboratoire de Physique Moléculaire et Applications, CNRS, Bât. 350,
91405 Orsay Cedex, France, e-mail: guelac@lpma.u-psud.fr*

Abstract

Infrared absorption spectra of the halogen nitrates ClONO$_2$ and BrONO$_2$
have been measured using the high-resolution step-scan Fourier-Transform
Spectrometer at LPMA in Orsay. The spectra were used to determine infrared
band centers of all fundamentals, except for the low-lying v_9 band (torsion)
of BrONO$_2$. For ClONO$_2$, spectra of isotopically pure ^{35}ClONO$_2$ allowed to
determine isotopic shifts of several vibrational frequencies.

Using this infrared data together with previously published spectroscopic
information (molecular structure, centrifugal distortion constants of ClONO$_2$,
mean vibrational amplitudes), the harmonic force fields of both molecules
were determined by least-squares calculations. The results are compared with
ab-initio calculations, other experimental data, and with the previously pub-
lished harmonic force field of FONO$_2$.

K25

THE HIGH-PRECISION LABORATORY FREQUENCY MEASUREMENTS OF THE INTERSTELLAR MOLECULES ROTATIONAL SPECTRA IN THE \70 ÷ 155 GHz FREQUENCY RANGE

E.A. Alekseev, O.I. Baskakov, S.F. Dyubko, M.N. Efimenko, V.A. Efremov,
V.V. Ilyushin and S.V. Podnos

Faculty of Quantum Radio Physics, Kharkov State University,
Svobody Sq. 4, 310077 Kharkov, Ukraine

A millimeter wave range radiospectrometer have been created and an frequencies of the rotational spectra lines were measured with high accuracy $\Delta v \le 1 \div 3$ kHz in the $53 \div 155$ GHz frequency range to the following molecules, which are interesting to the astrophysics: CH_3OH (68); CH_3OD (10); HCOOH (21); C_2H_5OH (72); CH_3CHO (46); $^{32}SO_2$ (75); $^{34}SO_2$ (25); OCS (15); CH_3NH_2 (31); $^{32}SO_2$, $v=1$ (15); $HCONH_2$ (17); H_2CCHCN (95); N_2H_4 (22); NH_2OH (12). The number of the measured frequencies of the absorption lines are given in the brackets.

The report presents a description of the used equipment, the measurement procedure justification including Lamb-deep technique, the spectra recording samples and the measurement treatment i.e. solving of the direct and the inverse problems.

K26

HIGH-RESOLUTION FOURIER-TRANSFORM INFRARED SPECTROSCOPY OF THE ν_4 AND $2\nu_4$ BANDS OF $CH_2=CHF$

A. De Lorenzi, S. Giorgianni, and P. Stoppa

Dipartimento di Chimica Fisica, Università di Venezia,
Dorsoduro 2137, I-30123 Venezia, Italy

The infrared spectra of vinyl fluoride have been investigated at a resolution of about 0.002 cm^{-1} in the ν_4 (1656 cm^{-1}) and $2\nu_4$ (3300 cm^{-1}) regions employing the Bruker IFS 120 HR Fourier Transform spectrometer at Giessen University.

$CH_2=CHF$ is a planar near-prolate molecule ($\kappa = -0.945$) belonging to the symmetry point group C_s; the vibrations examined are of symmetry species A' and the expected **a/b** hybrid bands show a prevalent contribution of the **a**-type component.

The vibrations investigated have been found affected by different perturbations with nearby states ($\nu_4/\nu_8+\nu_{12}/2\nu_9+\nu_{12}$; $2\nu_4/\nu_4+\nu_8+\nu_{12}/2\nu_6+\nu_{12}/\nu_6+\nu_7+\nu_{11}$), and the interaction mechanisms are mainly consistent with the first-order **b**-type Coriolis resonances. For the ν_4 fundamental, observed irregularities were satisfactorily interpreted by resorting to reduced energy level schemes computed in the prolate symmetric top limit; crossings for low K_a values have also been identified.

The rovibrational analysis of the bands examined was performed following standard procedures and using the Watson's A-reduction Hamiltonian in the I^r representation. The identified transitions led to the determination of a set of effective constants for the ν_4 and $2\nu_4$ vibrations.

Details of the interpretation and results obtained from the analysis will be presented.

K27

FERMI RESONANCE AND CORIOLIS COUPLING BETWEEN ν_5
AND $2\nu_6$ IN $CH_2{}^{35}ClF$

S. Blanco, A. Lesarri, J. C. López, J. L. Alonso

Departamento de Química Física, Facultad de Ciencias, Universidad
de Valladolid, 47005 Valladolid, Spain

A. Guarnieri

Abteilung Chemische Physik im Institut für Physikalische Chemie
der Universität Kiel

The rotational spectra of $CH_2{}^{35}ClF$ in the vibrational excited
states $\nu_5 = 1$ and $\nu_6 = 2$ have been observed in the frequency region 8-
250 GHz. Measurements of ^bP, ^bQ and ^bR branch transition frequencies
up to $J = 60$ have been carried out using FT-MW, Stark modulation and
millimeter-wave source modulated spectrometers. From infrared data
these states are predicted to be close to a third rank degeneracy ($2\nu_6$-
$\nu_5 = 10$ cm^{-1}) and both a Fermi resonance and a third rank Coriolis
resonance between them have been considered in the analysis of the
rotational spectra. The ^{35}Cl quadrupole coupling constants have been
also determined from the analysis of the hyperfine structure for both
vibrational states.

K28

GAS PHASE INFRARED SPECTRA OF AROMATIC MOLECULES . FORCE FIELD AB INITIO CALCULATION AND COMPLETE SPECTRUM ASSIGNMENT.

E. Cané, P. Palmieri, R. Tarroni and A. Trombetti
Dipartimento di Chimica Fisica e Inorganica Viale Risorgimento 4, 40136
Bologna Italy.

The gas phase infrared spectra of naphthalene-h_8, naphthalene-d_8 and of 1-azaindolizine have been recorded from 200 to 3500 cm^{-1} using a DA8 Bomem interferometer and a multipass cell with a 4.8 m path length, at the resolution of 0.05 cm^{-1}. To enhance the vapor pressure of these compounds the sample cell has been heated up to 60 ºC and to 80 ºC for naphthalene and 1-azaindolizine , respectively.

To assign the fundamental vibrations of 1-azaindolizine and to complete the assignment of the normal modes of naphthalene-h_8 and -d_8 we compared the experimental band frequencies and intensities to the theoretical ones from ab initio calculations.

The harmonic force field of naphthalene and 1-azaindolizine have been computed at the theoretical equilibrium geometry with the Hartree Fock Self Consistent Field (HF-SCF) method, using a standard set of 6-31G** orbitals. To remove the main limitations of HF theory we applied scaling factors to the harmonic force field converted to internal coordinate, according to the Scaled Quantum Mechanical (SQM) method. The scaling factors were determined by fitting the theoretical to the experimental spectra of parent molecules, which are benzene for naphthalene and pyridine and imidazole for 1-azaindolizine.

The harmonic force field of naphthalene has been also evaluated by Density Functional Theory (DFT), and compared to the former.

The root mean square deviation between the observed fundamentals and those computed with SQM method is 18 cm^{-1} for 1-azaindolizine, 22 cm^{-1} for naphthalene-h_8 and 17 cm^{-1} for naphthalene-d_8.The RMSD with DFT method is 32 cm^{-1} for naphthalene-h_8 and 19 cm^{-1} for naphthalene-d_8.

K29

Equatorial - Axial Conformational Equilibrium in 1-Fluoro-1-
silacyclobutane and Fluorocyclobutane.

S.Melandri and L.B.Favero
I.S.M. - C.N.R., Via Gobetti 101, I-40129 Bologna, Italy
W.Caminati and A.Maris
Dipartimento di Chimica dell' Università di Bologna "G.Ciamician" , Via
Selmi 2, I-40126 Bologna, Italy
M.Grosser and M.Dakkouri
Abteilung für Elektrochemie, Universität Ulm, D-890869 Ulm, Germany.

The microwave spectrum of 1-fluoro-1-silacyclobutane has been investigated in the 26- 40 GHz frequency range. The spectra of the equatorial and axial conformers and of several vibrational satellites, mainly belonging to the ring-puckering progression, have been assigned. The experimental results well agree with $6.31G^*$ calculations.

The axial conformer has been assigned also for fluorocyclobutane (only the equatorial species was assigned in a previous investigation [1]).

Rotational and centrifugal distortion constants, and vibrational spacings, obtained from relative intensity measurements for 1-fluoro-1-silacyclobutane and provided by a previous infrared study [2] for fluorocyclobutane, have been used to determine the potential energy function hindering the ring-puckering.

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K30

Investigation of the speed dependence of rotational relaxation using a microwave spectrometer with a circular waveguide: studies on nitrous oxide.

T.Köhler, H.Mäder and A.Schwenk

Institut für Physikalische Chemie, Universität Kiel, D-24098 Kiel, Germany

The experimental methods to determine rotational relaxation rates of molecules in the gas phase by using time-domain techniques in microwave spectroscopy have made considerable progress in recent years. The observation of transient emisson signals following pulsed excitation of the molecular sample provides direct information about the coherence decay rate T_2 which is directly related to the pressure-broadened halfwidth $\Delta\nu_{1/2} = 1/2\pi T_2$ of the line.

In view of the increasing importance of line broadening data for interpreting atmospheric spectra, an accurate knowledge of the pressure and temperature dependence of line shape data is needed. Both results from experiments in the frequency and time domain have shown the importance of a speed dependence of T_2 rates which produce non-Voigt line shapes in the frequency domain. [1]

For our investigations we have constructed a microwave spectrometer in K-band (18 - 26.4 GHz) with a circular waveguide as sample cell. Thereby problems of a previously used bridge-type spectrometer with oversized rectangular waveguides like adjustment of the bridge and influence of cell attenuation is partially overcome.

The spectrometer was used to investigate rotational relaxation for the $J = 1 \rightarrow 0$ transition of nitrous oxide (N_2O). The temperature dependence of T_2-rate parameters for various mixtures with foreign gases has been investigated by means of transient emission signals. To describe our time domain signals a quadratic dependence of the T_2 rate on the speed of emitting molecules was taken into account and effects arising from the cell geometry were also considered.

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K31

CENTIMETER AND MILLIMETER-WAVE SPECTRUM
OF SELECTED ISOTOPOMERS OF ACRYLONITRILE.

^{14}N QUADRUPOLE AND SPIN-ROTATION CONSTANTS.
STRUCTURE DETERMINATION.

J.M. COLMONT, G. WLODARCZAK, I. MERKE[+]
Laboratoire de Spectroscopie Hertzienne, URA CNRS 249, Université de
Lille I, France
H.S.P. MÜLLER[*], E.H. TIEN, R.J. RICHARDS, M.C.L. GERRY
Department of Chemistry, the University of British Columbia, Vancouver,
Canada

Acrylonitrile $H_2C=CHCN$ has been the subject of extensive spectroscopic investigations. An ab initio structure as well as an experimental structure have been calculated (most of the relevant references can be found in Ref.(1)). In order to improve the experimental structure, we have completed the already well known spectrum of $H_2C=CDCN$, and undertaken the study of all the ^{13}C and ^{15}N isotopic species of $H_2C=CHCN$ and $H_2C=CDCN$.

Both a and b type transitions have been measured in the frequency range 5-210 GHz. Accurate rotational and centrifugal distortion constants obtained from fits using the standard Hamiltonian of Watson, permit us to determine various types of molecular structure and to compare them.

Several of the transitions between 5 and 26 GHz were precisely measured with a microwave Fourier transform spectrometer. They also allowed ^{14}N quadrupole coupling constants and their variation with isotopomer to be determined.

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Present adress: +   Institut für Physikalische Chemie, Aachen, Germany
                   *   Jet Propulsion Laboratory, California Institute of
                       Technology, Pasadena, CA, U.S.A.

K32

PRESSURE BROADENING OF THE ν_3 BAND OF CO_2 AT CRYGENIC TEMPERATURES

D. Newnham, M. Page, and J. Ballard

Rutherford Appleton Laboratory,

Chilton, Didcot, Oxon, OX11 0QX, U.K.

He-, Ar-, N_2-, and air- broadening coefficients at 100 K were measured for P- and R- branch lines in the ν_3 band of CO_2 vapour. The Bruker IFS 120 HR Fourier transform spectrometer at RAL was used to record high resolution infrared absorption spectra of CO_2 vapour under 100 hPa fixed-pressure flow conditions in a liquid-nitrogen cooled collision cooling gas cell.[1] Under these experimental conditions, quantitative spectroscopy of supersaturated vapour phase CO_2 was possible. Clustering to form CO_2 aerosol also occurred, and the observations indicate that the fraction of cluster phase CO_2 is dependent on the broadening gas. Line broadening parameters, b_L, were calculated using the DECOMP program of Brault and Abrams.[2] Temperature dependent factors n of the pressure broadening were calculated using the new data together with literature data obtained at higher temperatures, and compared with the factors derived from theoretical models.

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K33

THE FIRST OBSERVATION OF FIELD FREE
$\Delta l = 2$, $f - e$ TRANSITIONS IN HCN

A.Maki,[w] W. Quapp,[l] S.Klee,[g] G.Mellau,[g]

[w]15012 24 Ave. S. E., Mill Creek, WA 98012, U.S.A.

[l]Mathematisches Institut, Universität Leipzig,
Augustus-Platz, D-04109 Leipzig, Germany

[g]Physikalisch-Chemisches Institut, Justus-Liebig-Universität
Heinrich-Buff-Ring 58
D-35392 Gießen, Germany

We have measured the intensities of the $\Delta l = 2$, $e - e$ and $f - e$ transitions 02^20-00^00, 12^20-00^00, and 02^21-00^00. The $e - e$ transitions are stronger than the $f - e$ transitions and get most of their intensity through the l−type resonance with the nearby allowed $\Delta l = 0$ transitions. For the $e - e$ transitions there is also a weak intensity contribution from a Coriolis interaction with more distant π levels. This Coriolis interaction is the dominant source of intensity for the $\Delta l = 2$, $f - e$ transitions.

It is shown that the intensity of the $02^{2f}0$-00^00 Q-branch transitions comes from the Coriolis interaction between the $02^{2f}0$ and $01^{1f}0$ levels which are separated by about 712 cm^{-1}.

Similar transitions have been observed for $H^{12}C^{15}N$.

K34

LINE SHIFT AND LINE ASYMMETRY
INTERDEPENDENCE
FOR THE H_2O SPECTRL LINES

L.I.Nesmelova, Yu.N.Ponomarev, O.B.Rodimova, S.D.Tvorogov

Institute of Atmospheric Optics, Tomsk, 634055, Russia

It was known[1] that the analysis of matrix elements of the relaxation operator as analytical functionsallows one to relate the asymmetry of line wings and the line shift. The relationship at hand follows from the dispersion relations between real and imagine parts of coefficients of the exact kinetic equation describing the line shape. Some qualitative conclusions were reached about spectral line shape starting from the experimental line shifts in the 4.3 μm CO_2 band[2] .

In this paper the experimental data on the H_2O line shift and asymmetry obtained by using the laser spectroscopy methods[3-5] are examined to confirm the aforementioned theoretical considerations. It is shown that qualitative conclusions on the presence of the line shape asymmetry for the lines exhibiting the strong line shift and the sign of the deviation of the line shape from the Lorentzian one agree quite well with measured values.

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K35

H$_2$O BROADENED BY CO$_2$ FOR APPLICATION
TO PLANETARY ATMOSPHERES

R. R. Gamache and S. P. Neshyba
University of Massachusetts Lowell
Center for Atmospheric Research
450 Aiken Street
Lowell, MA, 01854 USA

J. J. Plateaux, A. Barbe, L. Régalia
Laboratoire de Spectrométrie Moléculaire et Atmosphérique
Université de Reims
U. R. A. CNRS 1434, 51062 Reims Cedex, France
and
J. B. Pollack
Space Science Division
NASA-Ames Research Center
Moffett Field, CA 94035-1000

Measurements of CO$_2$-broadened halfwidths of 31 transitions belonging to the ν_1, $2\nu_2$, and ν_3 bands of water vapor were made at T=294.4 K. Calculations following the formalism of Robert and Bonamy with an electrostatic and atom-atom interaction potential and dynamics correct to second order in time were done for 562 transitions relevant to the 1-2.5µm window region. The calculations were compared with the measurements made in this work, a recent study by Langlois et al.[2] and an earlier work by Varanasi et al.[2] The calculations compared with experiment show average percent differences of +12, 1.5, and -8, respectively for the works listed above. Unfortunately there are no common lines measured by the different groups so a direct comparison of the measurements is not possible. Calculations of the temperature dependence of the halfwidths were made for 34 transitions. The temperature dependence of the halfwidths determined from theory and the measurements of Langlois et al. agree reasonably well with two exceptions.

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K36

A HIGH PRECISION TECHNIQUE FOR PRESSURE LINE SHIFTS MEASUREMENTS: APPLICATION TO NH_3 AND HCN

F. RAYNAUD, A. BABAY, V. LEMAIRE,

B. LEMOINE

Laboratoire de Spectroscopie Hertzienne

Associé au CNRS, URA-249 Université de Lille I

59655 Villeneuve d'Ascq Cedex, France

We have developped a new method for pressure line shift measurement in which the laser is frequency stabilised on the absorption peak of the molecular line under study.

In this technique, pressure induced line shifts entail frequency drifts of the stabilised laser : they are monitored thanks to a reference cell filled with the same active gas set at a fixed pressure which acts as a frequency discriminator. This experimental scheme avoids any reference to absolute or secondary frequency standards and directly gives the pressure induced frequency shifts.

With our diode laser spectrometer, pressure induced line shift parameters lower than 10 kHz/Torr with a 2 kHz/Torr accuracy where observed on the v_2 and the $2v_2$-v_2 band of NH_3 using a working pressure range of 10 Torr only. As an application, we considered some pressure line shifts of the v_2 bands of pure HCN and induced by H_2 and He.

K37

HIGH RESOLUTION UV SPECTROSCOPY OF PHENOL AND THE HYDROGEN BONDED PHENOL/WATER CLUSTER

GIEL BERDEN, W. LEO MEERTS,
MICHAEL SCHMITT, KARL KLEINERMANNS

Phenol and the hydrogen bonded Phenol$(H_2O)_1$ cluster have been studied by high resolution fluorescence excitation spectroscopy. The $S_1 \leftarrow S_0$ 0^0_0 vibronic transitions of the monomer and cluster were observed. All lines in the monomer spectrum are split by 56 ± 4 MHz due to the internal rotation of the OH group around the C-O bond. The rotational constants for the monomer were found to be A"=5650.452 MHz, B"=2619.190 MHz, C"=1789.843 MHz and A'=5313.6 MHz, B'= 2620.5 MHz; C'=1756.7 MHz, simulated with a rotational temperature of 5K

The region of the 0,0 transition of Phenol$(H_2O)_1$ shows two distinct bands which are 0.85 cm^{-1} apart. The analysis of both bands showed, that they arise from the vibrational/torsional motion, which interchanges the two equivalent H-atoms in the H_2O moiety of the cluster. This assignment was further confirmed by spin statistical considerations, which led to the inevitable conclusion, that the cluster has a symmetry plane bisecting the water moiety. A barrier of 140 cm^{-1} could be estimated for the electronic ground state and 120 cm^{-1} for the electronically excited state. The analysis of the rotational constants of the cluster yielded a O-O distance of the hydrogen bond of 2.865 Å in the electronic ground state and 2.824 Å in the electronically excited state.

K38

Diode Laser Spectra of Ar–CH$_4$ Complexes in the 7 μm
Region Observed with a New Double Modulation Technique

I. Pak[1,2], M. Hepp[1], D. Roth[1], and G. Winnewisser[1]

[1]*I. Physikalisches Institut, Universität zu Köln,
50937 Köln, Germany*

[2]*Institute of Spectroscopy, Russian Academy of Science,
142092, Troitzk, Moscow Region, Russia*

We have detected for the first time absorption spectra of Ar–
CH$_4$ complexes near the band center of the ν_4 band of CH$_4$ at 1304
cm^{-1} in a supersonic jet. About 50 new lines have been recorded.
For the detection of these spectra a new modulation technique has
been developed. A twofold modulation is applied to the absorption
signal. The pulsed operation of the jet yields a strong reduction of
disturbing interference fringes. A 10 kHz modulation of the laser
wavelength effectively reduces the low frequency laser excess noise.
The supersonic jet is produced with a high repetition (80 Hz) slit
nozzle, which increases the absorption path length through the
jet and strongly reduces the width of absorption lines. A detailed
description of our spectrometer will be presented together with
the recorded spectra of Ar–CH$_4$.

K39

HIGH RESOLUTION SPECTROSCOPY OF METHYL IODIDE USING A NOVEL DOPPLER-FREE TECHNIQUE

S.Carocci, A.DiLieto, A.Menciassi, P.Minguzzi, F.Quochi, and M.Tonelli

Dipartimento di Fisica dell'Università,
Piazza Torricelli 2, I-56126 Pisa, Italy

A new experimental method for high resolution spectroscopy has been recently introduced[1] for the study of molecular spectra. It can be described as a new version of the classical technique of double resonance and it gives access to Doppler-free measurements, with the possibility of selecting an arbitrary velocity class.

The principle is the old one of studying two coupled transitions in a three-level system. We use a pump laser to modify the population of the shared level and a probe radiation which propagates collinearly with the pump beam. The pump is modulated and the probe transmission is synchronously detected: therefore the probe samples only the velocity class selected by the pump. If the probe and/or the pump are reflected back, a Doppler-split doublet is observed and the doublet separation gives a direct calibration of the velocity scale.

We present the application of this method to the study of the electric dipole moment of methyl iodide in the excited vibrational state. The first measurements were performed on the $J = 10 \rightarrow 9$, $Kl = 9$, $F = 15/2 \rightarrow 13/2$ hyperfine component (the weaker of the multiplet) and the preliminary experimental results yield $\mu_o = 1.631\,(1)D$ for the $\nu_6 = 1$ state. This value is slightly smaller (about 0.6%) than for the ground state, and this behaviour is consistent with that observed for other CH_3X molecules.

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K40

INTRACAVITY LASER SPECTROSCOPY OF EXCITED ATOMS AND MOLECULES

V. Serdyukov, L. Sinitsa, Yu. Poplavskii, and A. Tobolkin
Institute of Atmospheric Optics, 634055 Tomsk, Russia

Intracavity Laser (ICL) Spectroscopy owing its high sensitivity to absorption, amplification, and small size of investigated volume is a perspective method for investigation of atoms and molecules under condition of different external exitations.

ICL-spectrometers based on Nd-glass and dye broad-bands lasers have been designed with pulse duration 2000 and 100 microsecond, respectively. It allows us to record such small absorption or amplification coefficients as $5 \cdot 10^{-9}$ and $10^{-7} cm^{-1}$ that corresponds to 500,000 and 10000 path length of traditional spectroscopy. There were used different techniques in our experiments for exciting molecules and atoms such as heating up to 1200 K, atomization with a laser, hollow cathode atomization, and excitation with a discharge plazma.

Large number of absorption and emission lines were recorded in atomic and electronic molecular spectra. The complicated character of ICL-spectra is connected with the fact that broad-band laser provides the realization of conditions for laser generation in a wide region:

"COEFFICIENT OF AMPLIFICATION = COEFFICIENT OF RESONATOR LOSSES"

As a result, any absorption (emission) line with K_{abs} (K_{amp}) more than $10^{-7} cm^{-1}$ inside the resonator cavity leads to the deep dips (sharp peaks) in spectrum of laser generation.

Results obtained in this investigation were used to measure low concentrations of atoms. For example, detection limit for U-atom is $10^7 atoms/cm^3$.

K41

Saturation Spectroscopy near 3000 cm^{-1} using a Frequency-Offset-Locked CO-Overtone Laser Sideband Spectrometer

M. Mürtz, B. Frech, P. Palm, M.H. Wappelhorst, W. Urban

Institut für Angewandte Physik der Universität Bonn

Wegelerstraße 8, D-53115 Bonn, Germany

J. Legrand, F. Herlemont

Laboratoire de Spectroscopie Hertzienne, Université de Lille

F-59655 Villeneuve D'Ascq Cedex, France

In recent years, the CO-overtone ($\Delta v = 2$) laser[1] has proved to be a useful source for molecular spectroscopy in the spectral region around $\lambda = 3$ μm. Here we present an application to high-accuracy saturation spectroscopy. In a first step, the laser frequency is stabilized in a frequency-offset locking (FOL) scheme on combination frequencies of two CO_2 laser standards. This FOL technique allows us to sweep the laser frequency in a well-defined and linear manner with very high frequency accuracy. To demonstrate the system performance we employed it for sub-Doppler spectroscopy of OCS utilizing a pump-and-probe setup. The frequency measurement of the Lamb-dip center showed a reproducibility of better than ± 10 kHz, the absolute accuracy is about 50 kHz (i.e. $\Delta\nu/\nu = 5 \cdot 10^{-10}$).

In a second step, we have combined the CO-overtone laser with microwave sideband generation in a CdTe crystal in order to increase the tuning range of the laser lines. The modulator generates tunable sidebands in the range of 8 to 18 GHz with an efficiency in the order of 10^{-3}. Through the combination of the sideband technique with the FOL scheme we obtain laser radiation showing wide tunability as well as excellent frequency stability and calibration. This enables us to make sub-Doppler heterodyne frequency measurements on several calibration gas molecules like OCS, CO_2, N_2O, HCN, in the mid-IR region of 75-114 THz (2500-3800 cm^{-1}). We report the latest results of these measurements which are in progress at present.

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K42

APPLICATION OF OROTRON INTRACAVITY MILLIMETER-WAVE SPECTROMETER FOR GAS ANALYSIS

B.S.Dumesh, V.D.Gorbatenkov and L.A.Surin
Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitzk,
Moscow region, Russia

Millimeter-wave spectrometer is proposed for multicomponent analysis on content of molecular impurities in the air and water vapor. The operation principle is absorption spectroscopy of molecules placed into a high quality ($Q=10^4$) resonator of millimeter-wave generator orotron [1]. Spectrometer operates with frequency or Stark modulation and has sensitivity about $(2-5)\times10^{-10}$ cm^{-1}. The wide spectral region of one device (90-160 GHz) makes it possible to measure spectra of overwhelming majority of molecules. Spectral resolution is limited by Doppler broadening and ensures accurate identification and selectivity of analysis. High sensitivity gives the detection limit 0.01-0.1 ppm for molecules with dipole moment about 1 D with time of measurement 1 min without preliminary enrichment of analyzed mixture. Owing to small expenditure of sample 0.1-1 cm^3/min under operating pressure 0.1-1 Torr the spectrometer may be used as a sensitive element of gas chromatographs. Preliminary measurements of a number of organic impurities (methanol, acetone, chloroform) in a water solution have shown the detection limit about 10^{-7} by volume concentration.

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K43

Precise Line Shape Measurements by Tunable Diode Laser

A.I.Nadezhdinskii

General Physics Institute, Russian Academy of Sciences,
Moscow

Precision limitations of Tunable Diode Laser Spectroscopy
(TDLS) are analyzed related to precise line shape measurements.
Different processes (baseline, optical zero, nonlinearity, laser
noise, etc.) are considered affecting experimental accuracy.
Analytical expressions were derived for different error sources.
Experimental procedure and data processing algorithm is
proposed to minimized the error of line shape parameters
determination. It was shown that relative intensity measurements
can be accurate within 0.3%. Difference between "hard" and
"soft" collision models was distinguished experimentally leading
to ability of determination of physically meaning collision
parameters from spectral line shape measurements.

L1

Spectroscopy and reactions in (halogenated-Benzene)-(NH$_3$)$_n$ clusters

C. Jouvet, S. Martrenchard-Barra, C.Dedonder-Lardeux, D. Solgadi,
P. Millié*, V. Brenner*

Laboratoire de photophysique moleculaire du CNRS
Bât 213, Université de Paris sud
91405 Orsay, France
* DRECAM/SPAM, CEN Saclay
91190 Gif sur Yvette, France

    The reactions of halogenated benzene NH$_3$ cluster ions, pioneered by B. Brutschy[1], are fascinating systems since for a given excitation energy, different reactions occur at different rates.Moreover the reactivity changes with the NH$_3$ cluster size. As an example, the reaction in 1-4 fluoroChloro benzene (NH$_3$)$_{1,2}$ leads to :

α)Cl elimination leading to the formation of Fluoroanilinium: F-C$_6$H$_4$-NH$_3{}^+$

β) HCl elimination leading to the formation of Fluoroaniline$^+$: F-C$_6$H$_4$-NH$_2{}^+$

γ) HF elimination leading to the formation of Chloroaniline$^+$: Cl-C$_6$H$_4$-NH$_2{}^+$

    Combining experimental techniques and calculations allows to disentangle the reaction mechanisms.

    From the S$_0$-S$_1$ REMPI vibrational and rotational spectroscopy and hole burning experiments the presence of different isomers can be evidenced and is used as calculations bench-marks.

    Ionization thresholds and reaction products thresholds are measured with two color-two photon techniques and lead to the barrier heights evaluation.

    The reaction times are studied with two methods : pulsed field extraction in a time of flight mass spectrometer is used for slow reaction and laser depletion technique for fast reactions.

    At last using synchrotron combined with supersonic expansion one can perform TPEPICO experiments (Thresholds PhotoElectrons PhotoIons COincidences) and define properly the relationship between the energy content in the ions and the reaction channels.

    A reaction mechanism can be deduced in combining all these experimental results with the gas phase collisional data and the calculations.

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L2

SPECTROSCOPY OF THE EARTH'S STRATOSPHERE: MEASUREMENTS OF THE HO$_X$, NO$_X$, AND CL$_X$ RADICAL CHEMISTRIES

K. Chance

Harvard-Smithsonian Center for Astrophysics,
60 Garden Street, Cambridge, MA 02138, USA

The Smithsonian Astrophysical Observatory far infrared balloon-borne Fourier transform spectrometer (FIRS-2) measures concentration profiles of trace gases in the earth's stratosphere. Measurements are made in the limb geometry using thermal emission from 80-210 cm^{-1} and 350-700 cm^{-1}. OH, HO$_2$, H$_2$O, H$_2$O$_2$, O^{3}P (thermospheric), O$_2$, O$_3$, HCl, HF, HBr, ClNO$_3$, HOCl, HOBr, CO, CO$_2$, N$_2$O, NO$_2$, HNO$_3$, and HCN are currently measured as functions of altitude and time. This paper briefly describes the instrument and the atmospheric measurements and concentrates on the development of underlying spectroscopy for the prediction and analysis of spectroscopic features. Other examples of current problems in the application of spectroscopy to atmospheric measurements will also be briefly described. These include the spectroscopic measurement from space of stratospheric OH, tropospheric ozone, and cloud height and coverage parameters.

M1

An *Ab Initio* Study on the Equilibrium Structure
and Torsional Potential Energy Function
for Hydrogen Peroxide and Dinitrogen Tetroxide

J. KOPUT

Dept. Chemistry, Adam Mickiewicz University, Poznań, Poland

The molecular parameters of hydrogen peroxide, H_2O_2, and dinitrogen tetroxide, N_2O_4, have been determined in large-scale *ab initio* calculations using the correlation-consistent basis sets of double- to quadruple-zeta quality (cc-pVDZ to cc-pVQZ).

The calculations for H_2O_2 were performed using the coupled-cluster method, CCSD(T). With the cc-pVQZ basis set, the equilibrium structural parameters are determined to be: $r(OO) = 1.4525$ Å, $r(OH) = 0.9627$ Å, $\angle(OOH) = 99.91°$, and $\angle(HOOH) = 112.46°$. The torsional barriers at the *trans* and *cis* conformations are found to be 377 and 2545 cm^{-1}, respectively.

The calculations for N_2O_4 were performed using the multiconfigurational second-order perturbation method, CASSCF/CASPT2. With the cc-pVQZ and cc-pVTZ basis sets for nitrogen and oxygen, respectively, the equilibrium structural parameters are determined to be: $r(NN) = 1.7940$ Å, $r(NO) = 1.1906$ Å, and $\angle(NNO) = 112.55°$. The potential energy barrier at the staggered conformation is found to be 2313 cm^{-1}, and the binding energy of the NN bond is calculated to be 4616 cm^{-1} (13.2 kcal/mol).

M2

MMW SPECTROSCOPY OF REACTIVE SPECIES PRODUCED BY LASER PHOTOLYSIS

M. CORDONNIER, M. BOGEY, A. WALTERS, B. DELCROIX

Laboratoire de Spectroscopie Hertzienne
Université des Sciences et Technologies de Lille
59655 Villeneuve d'Ascq - FRANCE

Glow discharges in gas mixtures have been extensively used to produce reactive species for study by MMW and IR spectroscopy. The main advantage of discharges are their simplicity and the great variety of short-lived molecules that can be produced from a few simple precursors.

In practice, the large number of species created can sometimes be a disadvantage. Indeed, when too many species are produced simultaneously, their transitions overlap and lead to very congested spectra whose analysis is not trivial. It is often impossible to produce only a specific molecule in a plasma.

UV laser photolysis appears to be a powerful method to complement the use of discharges. High power coherent UV emissions can induce specific bond breaks in a molecule and thus generate particular chemical products with a high efficiency and selectivity.

In this experiment, we use a 30 W Lumonics pulsed excimer laser to produce reactive species by the photodissociation of a gas precursor. The UV laser beam propagates in a cell in a direction opposite to that of the probe beam of a MMW spectrometer. Specific acquisition techniques have been developed for the selective detection of observed lines corresponding to species of a given lifetime.

We recently obtained new results concerning the formation of SO by photodissociation of $SOCl_2$. Rotational transitions in the MMW range have been observed in several vibrational and electronic states.

This preliminary experiment will be followed by the study of reactive species of astrophysical and atmospheric interest.

M3

REMPI SPECTROSCOPY ON AlO

A. Marijnissen and J.J. ter Meulen
Dept. of Molecular and Laser Physics, University of Nijmegen
Toernooiveld, 6525 ED Nijmegen, The Netherlands

New vibrational levels up to $v=10$ of the D $^2\Sigma^+$ state of AlO have been measured by (1+1) one color REMPI showing stongly perturbed $v=8$, $v=9$ and $v=10$ vibrational levels. In addition (1+1) two color REMPI was used to determine the adiabatic ionization potential (IP) of AlO.

The AlO radicals are produced by a Smalley type laser ablation source and are detected by a Wiley - McLaren type time of flight mass spectrometer. The different vibrational levels up to $v=10$ of the D $^2\Sigma^+$ state are measured by (1+1) one color REMPI. In previous experiments[1] the lowest 4 vibrational levels of the D $^2\Sigma^+$ state were already observed. The $v=8$, $v=9$ and $v=10$ of the 7 new vibrational states turn out to be strongly perturbed. This pertubation shifts the $v=8$ state to the red, resulting in a much smaller energy difference between the $v=7$ and $v=8$ than expected. The $v=9$ state has not been observed, probably due to predissociation of this level. T he $v=10$ state is shifted to the blue. Ab initio calculations of Schamps[2] show that this pertubation can be attributed to a $^2\Sigma^-$ state which lies in the same energy region as the perturbed vibrational levels.

(1+1) two color REMPI is used to determine the adiabatic IP of AlO. The first transition is made to C $^2\Pi_{1/2}(v=1)$; via this state a second transition is induced to the region close to the IP of AlO. By monitoring the photoions as a function of the total laser energy a photo ionization efficiency (PIE) spectrum is recorded. From this the IP of AlO is determined to be 9.820 eV (79200 cm^{-1}), about 0.3 eV higher than the value known in literature derived from electron impact measurements[3] Ionization via the D $^2\Sigma^+$ ($v=4$) state resulted in a preliminary value for the IP between 80043 cm^{-1} and 80729 cm^{-1} from which we conclude that via this D $^2\Sigma^+$ ($v=4$) state we do not have acces to the ground state of the AlO-ion but to an excited state.

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[2]J. Schamps, *Chem. Phys.* **2** 352-366 (1973)

[3]D. L. Hildenbrand *Chem. Phys. Letters* **20** 127-129 (1973)

M4

ANALYTICAL TREATMENT OF HIGHLY EXCITED
VIBRATION-ROTATIONAL STATES OF DIATOMIC MOLECULES

A.V.BURENIN AND M.YU.RYABIKIN

Institute of Applied Physics, Russian Academy of Sciences,
46 Uljanov Street, 603600 Nizhny Novgorod, Russia

The previously developed approach [1] to the analytical treatment of the vibration-rotational spectrum of a diatomic molecule taking into account the asymptotic behavior of the nuclear interaction potential has essentially been generalized. The generalization is concerned with the construction of the perturbation series when using the screened Kratzer potential

$$U(r) = (A/r^2 - B/r) F(\mu r)$$

where r is the internuclear distance, $1/\mu$ is the characteristic spatial scale of the screening factor $F(\mu r)$ (the condition $\mu(2A/B) < 1$ is assumed to be fulfilled). The $1/N$ expansion method [2] is employed to solve the radial part of Schrödinger equation, the value $1/s_v \ll 1$ being chosen as the expansion parameter, where $s_v = [2mA/\hbar^2 + 1/4 + J(J+1)]^{1/2} + v + 1/2$ (m is the reduced mass of the molecule, v and J are the vibrational and rotational quantum numbers). The suggested approach permits to allow for the realistic behavior of the internuclear potential at $r \to \infty$ even in the zeroth-order approximation. Algebraic recurrence relations have been obtained for the coefficients of $1/s_v$ expansion in any order of smallness. The solution for the energy of any vibration-rotational level is represented as a rapidly convergent series analogous to the previously obtained one in the perturbed Kratzer model [1]. This series is proved to be valid for treating a discrete vibration-rotational spectrum up to the dissociation limit both for molecules with an infinite number of discrete levels and for the case of a finite discrete spectrum. An isotopic dependence of spectroscopic constants of the constructed series and their relation with the Dunham constants are determined. The relations obtained have been applied to joint fit of vibration-rotational spectra of various isotopomers of the HCl molecule in the ground electronic state in the energy range up to the dissociation limit E_D. It has been shown that the series constructed by us converges rapidly within the entire interval of energies, while the traditionally used Dunham series has a strongly marked limit of validity equal to 0.39 E_D.

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M5

SEVEN BaCl ELECTRONIC STATES
BY L.I.F.F.T.S.

M.Hafid, J.Vergès and C.Amiot

Laboratoire Aimé Cotton, C.N.R.S. II, Bât. 505, Campus d'Orsay, 91405
Orsay France

Laser-induced fluorescence was observed in the BaCl molecule using the Ar^+, Kr^+ ion laser radiations and several lines emitted by a monomode Ti:Sa laser. The spectra were recorded by high resolution Fourier transform spectroscopy. The following ten electronic transitions were analysed for vibrational levels up to v=20:

$$B^2\Sigma^+ \rightarrow X^2\Sigma^+$$

$$C^2\Pi \rightarrow X^2\Sigma^+, A'^2\Delta, A^2\Pi, B^2\Sigma^+$$

$$E^2\Sigma^+ \rightarrow C^2\Pi, B^2\Sigma^+$$

$$F^2\Sigma^+ \rightarrow C^2\Pi, A^2\Pi, B^2\Sigma^+$$
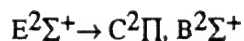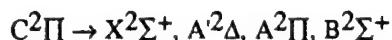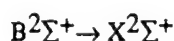
A fit, including simultaneously all the spectroscopic data for these transitions, has allowed the derivation of accurate molecular parameters for seven electronic states [1,2].

The three states $A'^2\Delta$, $A^2\Pi$ and $B^2\Sigma^+$ have then been considered as forming a 'd complex' in order to get more physically reliable constants [3]. The agreement of the derived constants with the recent theoretical predictions is very satisfactory [4].

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M6

THEORETICAL STUDY OF THE ELECTRONIC STRUCTURE OF Sr_2

N. Boutassetta, A.R. Allouche et M. Aubert-Frécon

Laboratoire de Spectrométrie Ionique et Moléculaire, CNRS et Université
Lyon I, Campus de la Doua, Bât. 205, F69622 Villeurbanne Cedex, France.

A theoretical study of the structure of all the molecular states dissociating into $Sr(5s^2)+Sr(5s^2 ; 5s4d ; 5s5p)$ has been performed. The method used is similar to that we previously used with success to describe the molecules BaH, BaLi, BaNa and Ba_2. The Sr atom is treated through a non-empirical effective potential. Molecular orbitals are obtained from a SCF calculation and a CI calculation is performed for the four active electrons using the CIPSI algorithm. Core polarization effects and core-valence correlation are taken into account by means of a core-polarization potential. Two sets of calculations have been performed corresponding to two different pseudopotentials for the Sr atom: one is a ten-electron effective potential as for the Ba atom and the other is a two-electron one, which was recently seen to be suitable to describe alkaline-earth atoms except Ba.

For the states $X^1\Sigma_g^+$ and $(2)^1\Sigma_u^+$ for which experimental data are available, the agreement with our predictions for spectroscopic constants is good.

State		$T_e(cm^{-1})$	$R_e(\mathring{A})$	$\omega_e(cm^{-1})$
$X^1\Sigma_g^+$	2-e pseudopotential	0	4.53	43.2
	10-e pseudopotential	0	4.51	37.4
	experiment	0	4.446	40.32
$(2)^1\Sigma_u^+$	2-e pseudopotential	17541	4.10	83.01
	10-e pseudopotential	17576	4.12	95.61
	experiment	17357.9	3.952	85.07

Energy curves and spectroscopic constants for all the bound states investigated will be presented.

M7

NEW RYDBERG-RYDBERG TRANSITIONS
OF THE ArH AND ArD MOLECULES

I. Dabrowski, D. Tokaryk, M. Vervloet[1],
R. H. Lipson[2], and J. K. G. Watson,
Steacie Institute for Molecular Sciences, National
Research Council, Ottawa, Ontario, Canada K1A 0R6

Previous analyses[3-5] of the spectra of ArH and (mainly) ArD are extended to other transitions using a case (d) Hamiltonian in which the rotational and centrifugal energies are expressed in powers of $\mathbf{R}^2$. The quantum numbers n and l, while not perfect, provide convenient labels for the states. The bands $5p \rightarrow 5s$ and $6p \rightarrow 5s$ have been analysed, and show that the small $np\pi - np\sigma$ separation found in the $4p$ complex[5] is accidental, the coefficients of λ^2 being 3.1, –126.7, and –70.1 cm^{-1} for $n = 4$, 5, and 6, respectively. The $3d$ complex has a wide splitting (σ, π and δ components at 16311, 13016, and 14637 cm^{-1} relative to $5s$ in ArD) with an almost pure fourth-rank tensor pattern. The bands $6s \rightarrow 4p$ and $8s \rightarrow 4p$ have also been analysed. The ArD transitions from $4f$ to $5s$, $3d\sigma$, $3d\pi$, and $3d\delta$ near 20682, 4371, 7666 and 6045 cm^{-1} give information on all components of the $4f$ complex, which is found to be a good example of Hund's case (d), with coefficient of λ^2 equal to 16.5 cm^{-1}. The quantum defects and other parameters are discussed in terms of the properties of the ArH$^+$ or ArD$^+$ core, including the l-mixing effects of the core electric dipole moment[6].

1. Present address: Laboratoire de Photophysique Moléculaire du CNRS, Bâtiment 213, Université de Paris-Sud, 91405 Orsay, France.

2. Present address: Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7.

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M8

FERMI RESONANCE AND SINGLET TRIPLET PERTURBATIONS IN THE SPECTRUM OF SINGLET METHYLENE

Alexander Alijah[2], Geoffrey Duxbury[1] Marcel van Gogh and Barry McDonald

1. Department of Physics and Applied Physics, Galsgow, Scotland. U.K.
2. Facultat fur Chemie, Universitat Bielefeld, D-4800 Bielefeld, Federal Republic of Germany.

Ever since the discovery and analysis of the red system singlet CH_2 by Herzberg and Johns this deceptively simple looking spectrum has provided a large variety of puzzles. This is due to three types of interactions between the rovibronic levels of CH_2:

Renner-Teller interaction between the $\tilde{a}$ $^1A_1$ and the $\tilde{b}$ $^1B_1$ states which correlate with a $^1\Delta_g$ state of the linear molecule.

Stretch-bend interactions within the $\tilde{a}$ and the $\tilde{b}$ states

Spin-orbit coupling between the $\tilde{a}$ and the $\tilde{b}$ states and the $\tilde{X}$ $^3B_1$ ground state.

Following initial work by Jungen we have developed and extension of the semirigid bender approach of Bunker to calculate the interplay between Renner-Teller and vibrational resonances in detail. We have called this approach the "Stretch-Bender "approach to the calculation of energy levels of triatomic molecules.

The basic idea is that if in the semirigid bender the bond length relaxes to follow the minimum on the potential energy surface, the effect of the stretch-bend coupling should be minimised in this basis. When only a few quanta of the stretching vibrations are excited via resonances, this should simplify the calculations compared to those using a full 3D basis.

We will give examples of the application of this approach to gain a better understanding of the spectrum of CH_2, including the most recent results from Sears and Dai's groups.

M9

ROTATIONAL ANALYSIS OF TWO ELECTRONIC TRANSITIONS
OF NiCl

C. Dufour and **B. Pinchemel**

Laboratoire de Dynamique Moléculaire et Photonique

Université de Lille I - UFR de Physique - Bâtiment P5

59655 Villeneuve d'Ascq Cedex, France

Michel Vervloët

Laboratoire de Photophysique Moléculaire

Université Paris XI - Bâtiment 213

91405 Orsay Cedex, France

High resolution Fourier Transform spectra of NiCl have been recorded from the emission of a flowing mixture of $NiCl_2$ heated to 600°C and argon at a pressure of 5 Torrs excited by a 2450 MHz electrodeless discharge. Despite the presence of numerous atomic lines it has been possible to observe a large number of ro-vibrational bands. Two of them have been rotationaly analysed. It turns out that, as observed in NiF, several electronic low lying states are involved in the transitions.

M10

GLOBAL ROVIBRATIONAL ANALYSIS OF CYANOGEN FLUORIDE (FCN)

K. Farkhsi, I. Dubois and H. Bredohl

Institut d'Astrophysique - Université de Liège

5 avenue de Cointe - B-4000 Liège

A. Fayt

Molecular spectroscopy laboratory - Université Catholique de Louvain

2 Chemin du Cyclotron - B-1348 Louvain-La-Neuve

The infrared absorption spectrum of FCN has been recorded in the region of 1200 to 7000 cm^{-1} with a Fourier Transform Spectrometer at an instrumental resolution of 0.0026 cm^{-1}. More than 20 000 rotational lines have been attributed to 130 bands.

After a band by band analysis of these transitions a global analysis of the electronic ground state has been performed including microwave, millimeter and submillimeter data. l-type and anharmonic resonances are taken into account in a one-step diagonalization. The least square procedure used, allows to determine a set of 100 zero field parameters; lines are recalculated within 10^{-4} cm^{-1}.

M11

A Dipole Moment Function for the Water Molecule Determined from Experimental Rovibrational Line Intensities in a Variational Approach

S.A.Tashkun, Vl.G.Tyuterev and P.Jensen

Institut of Atmospheric Optics SO RAN,Tomsk 634055, Russia;
Laboratoire de Spectrometrie Moleculaire et Atmospherique,
    Faculte des Sciences, B.P. 347, 51687 Reims, France;
FB 9 -Theoretische Chemie,Bergische Universitat-Gesamthochschule,
    D-42097 Wuppertal, B.R.D.

A simultaneous fitting of vibration-rotational line strengths of fundamental, overtone, combination and hot bands of the water molecule has been performed in order to determine the dipole moment function directly from observed infrared and microwave data.

In order to calculate vibration-rotational wave-functions and ro-vibrational transition moments the recent refined potential energy surface [1] for the electronic ground state of water molecule has been used which had been determined from the most extended set of experimental energies and transition frequencies for various isotopic species (120 vibration-rotation bands of 10 isotopomers).

The calculations are carried out with the Hamiltonian written in the MORBID form and the dipole moment function is represented by an expansion in bond length displacements for stretching coordinates and in cosine of the bending angle [2].

Preliminary comparison with *"ab initio"* intensity calculations as well as with"polyad-by-polyad" calculations based on effective Hamiltonians and effective dipole-moment operators will be discussed.

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M12

THE EMISSION SPECTRUM OF HOT WATER IN THE
REGION BETWEEN 370 and 930 cm^{-1}

Oleg L. Polyansky

*Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen,
Heinrich-Buff-Ring 58, D-35392 Giessen, Germany.*

Jennifer R. Busler, Bujin Guo, Keqing Zhang
and Peter F. Bernath

*Department of Chemistry, University of Waterloo,
Canada N2L 3G1*

A spectrum of the hot water molecule has been recorded in emission at a temperature of 1550° C in the region between 373 cm^{-1} and 933 cm^{-1}. More than 4000 pure rotational lines were observed with the strongest belonging to the ground state (000) and the first excited bending vibrational level (010). Transitions involving rotational quantum numbers J and K_a significantly higher than previously recorded have been assigned.

M13

INFRARED SPECTRA OF OZONE IN THE 4300 cm^{-1} REGION.
ANALYSIS OF THE $3v_1+v_3$ BAND INCLUDING
$2v_1+3v_2$ DARK BAND

O. Sulakshina, A. Barbe, Vl G. Tyuterev and J.J. Plateaux

G.S.M.A., U.A. CNRS D 1434

Faculté des Sciences

BP 347 - 51062 REIMS Cédex - France

The infrared spectra of $^{16}O_3$ has been recorded in the 4300 cm^{-1} region with a Fourier transform spectrometer at 0.008 cm^{-1} resolution, using a White type cell $\ell = 32.16$ m filled with 42.8 Torr O_3. This spectral region corresponds to the $3v_1+v_3$ band, which has never been observed so far. The assignment of this band has been performed up to J = 43 and $K_a = 13$. To correctly reproduce the obtained energy levels of $3v_1+v_3$, it has been necessary to introduce the 230 dark state, interacting through Coriolis resonance. With the Hamiltonian for these two interacting states, the fit on the 282 energy levels is 1.5 10^{-3} cm^{-1}, of the order of the experimental precision. Lines intensities of the $3v_1+v_3$ are measured and calculated.

TF Spectra of Isotopic Carbon Disulfide: the 3v$_3$ Band of $^{12}C^{34}S_2$ and $^{13}C^{32}S_2$

Ghislain BLANQUET[*], Jacques WALRAND[*],

Jean-François BLAVIER[+], Harald BREDHOL[+],

and Iwan DUBOIS[+].

[*] Laboratoire de Spectroscopie Moléculaire, Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles, B-5000 Namur, Belgium

[+] Institut d'Astrophysique, Université de Liège, 5, avenue de Cointe, B-4200 Liège, Belgium.

By Fourier transform spectroscopy, spectra have been recorded at the University of Liège for isotopically enriched carbon disulfide $^{12}C^{34}S_2$ and $^{13}C^{32}S_2$ in the region of the 3v3 band with a resolution of 4. 10^{-3} cm^{-1}.

The following transitions have been observed:

$^{12}C^{34}S_2$		$^{13}C^{32}S_2$	
	00^03-00^00		00^03-00^00
	01^13-01^10		01^13-01^10
	10^03-10^00		10^03-10^00
	02^03-02^00		02^03-02^00
	02^23-02^20		02^23-02^20
	03^13-03^10		03^13-03^10
	03^33-03^30		
$^{12}C^{32}S^{34}S$	00^03-00^00	$^{13}C^{32}S^{34}S$	00^03-00^00
	01^13-01^10		
$^{12}C^{33}S^{34}S$	00^03-00^00	$^{13}C^{32}S^{33}S$	00^03-00^00
	01^13-01^10		
$^{12}C^{34}S^{36}S$	00^03-00^00		
	01^13-01^10		

The data were fitted and new molecular constants determined.

M15

A NEW ROVIBRATIONAL ANALYSIS OF THE ν_2 AND ν_5 INFRARED BANDS OF $H_3Si^{79}Br$

A. Ceausu and G. Graner

LPMA, Université Paris Sud, Bât. 350, 91405 Orsay, France.

H. Bürger

Anorganische Chemie, FB9, Universität Gesamthochschule,

42097 Wuppertal, Germany.

P. Pracna

J. Heyrovský Institute of Physical Chemistry, Dolejškova 3,

18223 Prague 8, Czech Republic.

A high-resolution Fourier transform spectrum (resolution 0.0022 cm^{-1}) of monoisotopic $H_3Si^{79}Br$ in the region 830-1050 cm^{-1} was used to analyze the ν_2 (A_1) and ν_5 (E) fundamental bands, improving a former work[1]. 4338 transition wavenumbers for ν_2 and ν_5 were fitted, together with 632 upper state energies of $\nu_3=2$, deduced from the previously determined transitions[2] of $2\nu_3-\nu_3$ and ν_3. The model included two global resonances, the x, y Coriolis resonance between ν_2 and ν_5 and the $\ell(\pm2, \pm2)$ resonance within ν_5, and also three weak and local resonances: a Coriolis-type resonance between ν_5 and $2\nu_3$, an r-type resonance between ($k\ell=2$) and ($k\ell=-3$) of ν_5 and an $\ell(\mp1, \pm2)$ resonance between the ($k\ell=1$, $A^{\pm}$) levels of ν_5 and the (K=3, $A^{\pm}$) levels of ν_2. This last accidental resonance activates $\Delta K=\pm3$ transitions; five of them were included in the fit. This converges with a s.d. on residuals of 0.000123 cm^{-1}. A complete set of molecular parameters for all levels involved will be reported.

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M16

WATER VAPOR ABSORPTION IN A MILLIMETER WAVE ATMOSPHERIC WINDOW

A. Bauer, M. Godon and J. Carlier

Laboratoire de Spectroscopie Hertzienne

CNRS - Université de Lille I

59655 - Villeneuve d'Ascq Cédex - France

R.R. Gamache

Center for Atmospheric Research

Lowell - MA 01854 - USA

Laboratory studies have been performed in the millimeter wave spectrum of water vapor, at 239 GHz. This region constitutes a window for the earth atmospheric spectrum, and because it is simultaneous a large window for the CO_2 spectrum, it is also of interest for Venus and Mars spectroscopic investigations. A Fabry-Perot interferometer of high sensitivity ($Q \sim 10^6$) has allowed measurements of the absolute absorption of water vapor with its mixtures with N_2 and CO_2. Pressure and temperature dependences are obtained. The experimental data, especially for the $H_2O + CO_2$ mixture, are very different from models using the Van Vleck Weisskopf lineshape. In the case of a CO_2 mixture, this model involves new calculations of $H_2O + CO_2$ collisional line broadenings.

M17

Near infrared absorption of Ammonia at high pressure.

Line Lundsberg-Nielsen, Flemming M. Nicolaisen and J. Henningsen*

Danish Institute of Fundamental Metrology,
Bldg 307, Anker Engelunds Vej 1, DK-2800 Lyngby, Denmark

* *Institute of Chemistry, University of Copenhagen,*
Universitetsparken 5, DK-2100 Copenhagen, Denmark

Molecular absorption in the near infrared spectral region is caused by overtone- and combination transitions. Although they are usually several orders of magnitude weaker than the fundamental transitions, they are interesting for several reasons. They are important for atmospheric transmission in the near infrared and the availability of cheap, reliable diode lasers developed for communication purposes, make these transitions interesting for monitoring.

For both atmospheric monitoring and process control one must be concerned with the absorption at high pressure. Atmospheric transmission per definition relates to ambient pressure, and for monitoring purposes the sensitivity will increase with partial pressure due to more dominating wing contributions from lines centred far away from the monitoring frequency.

At 1000 mB $^{14}NH_3$ about 90% of the total absorption originates from the wings of distant absorption lines. The measured absorption is higher than predicted by a model calculation based on the absorption lines reported earlier [1] and [2].

Previous measurements were recorded at low pressure by FTIR at 0.005 cm^{-1} resolution and 237 cm pathlength. In order to incorporate lines below the detection limit of previous experiments we have improved the sensitivity of our earlier high-resolution measurements, by increasing the pathlength by an order of magnitude.

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M18

The Rovibrational Spectrum of AsF₃. A Combined High Resolution Infrared and Millimeterwave Study.

H. Bürger, J. Radtke, and H. ruland

Anorganische Chemie, FB9, Universität-Gesamhoschschule, D 42097 Wuppertal, Germany

P. Dréan and J. Demaison

Laboratoire de Spectroscopie Hertzienne, associé au CNRS, Bât. P5, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France.

Gas phase infrared spectra of the C_{3v} symmetric top arsine trifluoride have been recorded with a resolution of $2.5 - 5.0 \cdot 10^{-3}$ cm^{-1} in the regions of all fundamental bands : $v_1 - v_4$. Furthermore the millimeterwave spectra of the excited vibrational states $v_1 = 1$, $v_2 = 1$; 2, $v_3 = 1$, and $v_4 = 1$ have been measured in the range 100-470 GHz. Rotational parameters of all the vibrational states have been accurately determined by merge of the infrared and millimeterwave data.

For high-J rotational transitions, the splitting of the $K = 3$ lines was observed and analyzed. Comparison with the value previously determined for the ground state shows that the splitting constant h_3 seems to vary much with the vibrational state.

The vibrational wavenumbers are as follows: $v_1(A_1) = 740.57075(2)$, $v_2(A_1) = 337.79643(5)$, $v_3(E) = 702.56505(2)$ and $v_4(E) = 262.99420(2)$ cm^{-1}. Coriolis x, y resonance between v_1 and v_3 was considered. The ground state and equilibrium structures have been determined.

M19

FTIR STUDY OF THE SECOND STRETCHING

VIBRATIONAL OVERTONE SYSTEM OF $H_3{}^{70}$GeD:

EXAMPLE OF AN ALMOST ASYMMETRIC ROTOR BAND

Hans Bürger

Anorganische Chemie, FB 9, Universität Wuppertal,
D-42097 Wuppertal, Germany

Lauri Halonen

Laboratory of Physical Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1),
FIN-00014 University of Helsinki, Finland

The FTIR spectrum of monoisotopic $H_3{}^{70}$GeD near 6100 cm^{-1} was recorded with a resolution of ca. 0.012 cm^{-1}. A perpendicular-type band, $\nu_0(E)$ = 6129.441 cm^{-1}, is observed, which is unperturbed for $K' \leq 12$. Its rotational analysis reveals, in addition to rovibrational r and q resonance effects within the E vibrational state, a strong rovibrational α resonance perturbation by an almost degenerate perturber of A_1 symmetry, ν_0 = 6129.434 cm^{-1}. Owing to intensity perturbations the parallel component is very weak in spite of a transition moment ratio $\mu(E)/\mu(A_1)$ of ca. -2. The rovibrational energy level pattern is indicative of local mode behaviour of the $\Delta\nu_{(GeH)}$ = 3 state, in which Coriolis effects are almost absent and simple arithmetic relations between vibration-rotation parameters fulfilled. This gives rise to an excited state energy level pattern almost consistent with that of an asymmetric rotor.

M20

High-resolution FTIR study of the $\nu_1+\nu_5$, $\nu_2+\nu_3+\nu_4-\nu_3$ and

$\nu_3+\nu_4+\nu_5-\nu_3$ rovibrational bands of $CH_3{}^{79}Br$.

N.BEN SARI-ZIZI,Laboratoire de Spectronomie physique appliquée,

Faculté des Sciences, Université Mohammed V, B.P.1014,

Rabat(Agdal),Morocco.

C.ALAMICHEL, Laboratoire de Photophysique moléculaire du CNRS,

Bâtiment 213, Université Paris-Sud, 91405 Orsay Cedex,France.

The $\nu_1+\nu_5$ band of methyl bromide has already been studied, but only at low resolution so that only Q branches , and not J lines, had been observed, correctly assigned from ${}^PQ_1$ up to ${}^RQ_8$, the authors finding the $\Delta K=-1$ side much perturbed.

Using a much better spectrum recorded by G.GUELACHVILI (resolution of 0.006 cm^{-1}) with a sample of pure $CH_3{}^{79}Br$, we observed the J lines, but their assignment was quite difficult because they are very often overlapped by the much stronger lines of $\nu_2+\nu_4$ and $\nu_4+\nu_5$. Nevertheless it has been possible to assign the $K''.\Delta K =0$ to 9 and the $K''.\Delta K=-6$, -7 and -9 sub-bands through the combination differences relationships.

But we met two difficult problems:

- first, there are several Q branches on the $\Delta K=-1$ side which obviously do not belong to $\nu_1+\nu_5$. The $v_3=1$ level being well known, the combination differences relationships allowed to assign the $K''.\Delta K= -6$ to $+3$ sub-bands of the $\nu_2+\nu_3+\nu_4-\nu_3$ hot band, and also several sub-bands of $\nu_3+\nu_4+\nu_5-\nu_3 E$ which overlap $\nu_1+\nu_5$ on the $\Delta K=+1$ side.

-secondly, an anharmonic resonance connects ν_1 to $\nu_3+\nu_5+\nu_6$ A_1+A_2 (1) with a coupling about 3.8 cm^{-1}; then, the same interaction occurs between $\nu_1+\nu_5$ and both perpendicular components of $\nu_3+2\nu_5+\nu_6$. Unfortunately both interactions counterbalance each other except in the range between $K''\Delta K=-1$ and -5 where the upper levels of $\nu_1+\nu_5$ and of both perturbers cross altogether, which makes this part of the spectrum very complicated. However one ${}^PQ_1$ and ${}^PQ_2$ and two ${}^PQ_3$ and ${}^PQ_4$ have been surely assigned; the ${}^PQ_5$ has only been localized because it is too weak. The next step will be to attempt a fit over all the Q branch heads of $\nu_1+\nu_5$.

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M21

HIGH RESOLUTION ROOM TEMPERATURE STUDY OF THE $2\nu_1$-ν_1 ROVIBRATIONAL TRANSITIONS OF CH_4 BY STIMULATED RAMAN PUMPING - INVERSE RAMAN SPECTROSCOPY

D.Bermejo, **R.Z.Martinez** and **J.Santos**
Instituto de Estructura de la Materia, CSIC
Serrano, 123. 28006 - Madrid. SPAIN

J.P.Champion and **J.C.Hilico**
Laboratoire de Physique. URA CNRS 1796 Université de Bourgogne
6, Bd. Gabriel. 21000 Dijon. FRANCE

The high resolution Raman spectrum of the $2\nu_1$-ν_1 band of CH_4 has been obtained for the first time. A new technique has been used that allows room temperature conditions for this measurement. The spectrum is assigned and compared with theoretical calculations.

The experiments were carried out with a Raman-Raman double resonance technique: in a first step, the excited vibrational state $\nu_1=1$ is significantly populated by means of a stimulated Raman process, in which population is transferred from the ground to this excited vibrational state using two nanosecond laser pulses. One of these pulses has been previously generated from the other one with the use of a Raman shifter filled with CH_4 at high pressure. For the second step, inverse Raman spectroscopy is used to obtain a high resolution spectrum of transitions departing from the excited state. Between the two steps, a delay of several nanoseconds has been introduced to allow for rotational relaxation and to avoid Stark effect produced by the strong pump beams. With this setup, more than 20 lines of the $\nu_1=2 <- \nu_1=1$ band, with $J \leq 6$ have been observed and assigned for the first time.

A preliminary analysis of the spectrum has been done by fitting simultaneously the ν_1 and $2\nu_1$ bands using an isolated band model. The standard deviation achieved was close to the experimental one. However, the values anomalously large obtained for some high-order spectroscopic parameters suggest the need for a theoretical treatment within the polyad scheme of methane. Such a study is in progress.

M22

GROUND STATE AXIAL ROTATIONAL CONSTANTS

OF $^{12,13}CH_3I$ and $^{12,13}CD_3I$

M. Koivusaari, S. Alanko, J. Pietilä,

V.-M. Horneman, R. Paso, and R. Anttila

Department of Physical Sciences, University of Oulu

Linnanmaa, 90570 Oulu, Finland

There are two methods to derive the axial rotational constant A from rotation-vibration spectra for symmetric top molecules. First of them makes use of perturbation-allowed transitions. The other possibitlity is to combine the infrared spectra of a perpendicular fundamental ν_t, a hot band $\nu_{t'} + \nu_t - \nu_t$ and the combination band $\nu_{t'} + \nu_t$ (E). It is also possible to use an overtone instead of the combination, that means $t = t'$. By using the high resolution Fourier transform spectra recorded on the Bruker 120 HR spectrometer in Oulu we have made A_0 constant determinations for different isotopic forms of methyl iodide and applied both the methods mentioned above as follows:

	A_0 /cm^{-1}	$D_0^K/10^{-6}$	$H_0^K/10^{-9}$	Ref.
$^{12}CH_3I$				
pert. ν_5 / $\nu_3 + \nu_6$	5.173931(2)	87.36(5)		[1]
$\nu_6, 2\nu_6, 2\nu_6 - \nu_6$	5.173936(1)	87.63(3)	4.53(22)	[2]
$^{13}CH_3I$				
pert. ν_5 / $\nu_3 + \nu_6$	5.174258(4)	87.56(7)		[3]
$\nu_6, 2\nu_6, 2\nu_6 - \nu_6$	5.174266(3)	87.93(5)	4.91(27)	prelim.
$^{12}CD_3I$				
$\nu_6, \nu_5 + \nu_6, \nu_5 + \nu_6 - \nu_6$	2.596278(2)	20.77(4)	0.38(24)	[4]
$^{13}CD_3I$				
$\nu_6, \nu_5 + \nu_6, \nu_5 + \nu_6 - \nu_6$			in progress	

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M23

SUBDOPPLER STUDY OF THE $v_3 = 2$ STATE OF SF$_6$ BY IR-IR DOUBLE RESONANCE WITH A SIDEBAND SPECTROMETER

M.KHELKHAL, E.RUSINEK, J.LEGRAND AND F.HERLEMONT
Laboratoire de Spectroscopie Herzienne U.R.A.249
Université des Sciences et Techniques de Lille
59655 Villeneuve d'Ascq Cedex France.

AND

G.PIERRE
Laboratoire de Physique de l'Université de Bourgogne URA 1796
Théorie des systèmes moléculaires et des phénomènes non linéaires
6 Bd Gabriel 21000 Dijon France

The $v_3 = 2$ state of SF$_6$ has been investigated using two independantly tunable sidebands of a CO$_2$ laser. An electrooptic modulator, based on microstrip concept, is excited by a wave in the range $0 - 4$ GHz to create a sideband resonant with the cold band transition used as pumping radiation. A second electrooptic modulator working in the $8 - 18$ GHz range is used to monitor the disturbance in the $2\nu_3 - \nu_3$ band.

About 250 lines of both the cold band ν_3 and the hot band $2\nu_3 - \nu_3$ have been assigned on the basis of a calculated spectrum. Their frequencies have been determined with an accuracy better than 50 kHz.

The spectrum is analysed and the lines are fitted using an effective Hamiltonian developped through the 6th order for the Ground State, the 7th order for the $v_3 = 1$ state and the 4th for the $v_3 = 2$ state. The standard deviation is about a few tens kHz for ν_3 lines and about a few hundreds kHz for $2\nu_3 - \nu_3$ lines.

M24

Measurements of Ultraviolet-Visible Absorption Cross Sections of $BrONO_2$ (Bromine Nitrate)

B. DETERS, J. ORPHAL[†], AND J. P. BURROWS

Institute of Environmental Physics, University of Bremen, P.O. Box 330440, 28334 Bremen, Germany, e-mail: orphal@gomel.physik.uni-bremen.de

Abstract

$BrONO_2$ (Bromine Nitrate) is a molecule of potential interest for stratospheric ozone depletion chemistry. This species is a stable reservoir for both NO_x and BrO_x, and is formed by the gas-phase reaction between BrO and NO_2. Atmospheric photolysis rates and spectroscopic information can be obtained using laboratory UV-VIS cross section measurements.

We report measurements of $BrONO_2$ absorption spectra in the UV-VIS region with a diode-array grating spectrometer. The $BrONO_2$ sample was synthesized in our chemical laboratory using the reaction of Br_2 with $ClONO_2$, followed by distillation. The spectra were recorded using a White-type multiple-path absorption cell, made of quartz, and at different temperatures. The detector was a 1024-pixel diode array (OMA) controlled by a 386 microcomputer. Absolute $BrONO_2$ concentrations were determined using the rapid photolytical conversion of the molecules into Br_2, which can be quantified easily by its absorption around 400-420 nm.

M25

AMBIGUITY OF CORIOLIS PARAMETERS DESCRIBING THE $2\nu_5/\nu_4$ AND $\nu_4+2\nu_5/2\nu_4$ RESONANCE SYSTEMS OF HCNO.

K. Islami[1], R. Schermaul, G. Schulze, B.P. Winnewisser, and

M. Winnewisser

Justus-Liebig-Universität Giessen

Heinrich-Buff-Ring 58

D-35392 Giessen, Germany

Fulminic acid, HCNO, is an example of a quasilinear molecule. Many publications in the 25 years of its spectroscopic history have had as subject different aspects of its behavior. During the analysis of the spectra of HCNO we were able to observe and to analyze several accidental resonances. Some problems remained in the fits of data to an effective Hamiltonian of a linear molecule for the case of the transitions affected by Coriolis resonance. These discrepancies seem to be connected with the high correlations involving Coriolis parameters in the framework of the current model and with the fact that even in the case of the lowest resonance system $2\nu_5/\nu_4$ the two definable Coriolis parameters could not be fitted simultaneously. The aim of this work is to illuminate the high correlation of the Coriolis parameters describing the systems $2\nu_5/2\nu_4$ and $\nu_4 + 2\nu_5/\nu_4$ and the ambiguity in the determination of these parameters. The relation between the parameters of the first and second Coriolis resonance system will be discussed theoretically and tested with the experimental data. Some conclusions about the limits of the current model for describing such resonances will be made.

[1]PERMANENT ADDRESS: UNIVERSITY OF TIRANA ALBANIA

M26

HIGH-RESOLUTION INFRARED STUDY OF THE ν_3 AND ν_4 FUNDAMENTALS OF CF_2=CHF

R. Visinoni and S. Giorgianni

Università di Venezia

Dipartimento di Chimica Fisica

D. D. 2137, I-30123 Venezia, Italy

The infrared spectrum of CF_2=CHF has been investigated in the ν_3 ($\cong$ 1360 cm^{-1}) and ν_4 ($\cong$ 1265 cm^{-1}) regions, at a resolution of about 0.002 cm^{-1}, using a tunable diode laser spectrometer. Trifluoroethylene is a planar molecule belonging to the symmetry point group C_s and the ν_3 and ν_4 fundamentals of A' species give rise to *a/b* hybrid bands with a prevalent contribution of the *b*- and *a*- type components, respectively.

The ν_3 band is affected by first-order *b*-type Coriolis resonance with $\nu_{10} + 2\nu_{12}$ and $\nu_7 + \nu_{10}$ states, and the strongest interaction effect has been found for the $K_a' = 11$ and 12 levels. From the subband analyses of the ν_4 fundamental there is evidence that also this band is slightly influenced by Coriolis resonance, and the $\nu_8 + \nu_9 + \nu_{11}$ combination seems to be responsible for the observed perturbations.

The identified transitions, free of major resonance contribution, were fitted using the Watson's A-reduction Hamiltonian in the I^r representation, and a set of effective rotational and quartic centrifugal distortion constants was determined for both ν_3 and ν_4 vibrations. An investigation on the ν_5 fundamental, around 1170 cm^{-1}, is also in progress.

Experimental details and results from the analysis will be presented.

M27

ASSIGNMENT AND ANALYSIS OF THE ROTATIONAL SPECTRUM OF CH_2I_2

W.Caminati[a], P.Favero[a], Z. Kisiel[b], and L.Pszczółkowski[b]

[a]Istituto Chimico "G.Ciamician", Universita di Bologna,
Via Selmi 2, 40126-Bologna, Italy

[b]Institute of Physics, Polish Academy of Sciences,
Al.Lotników 32/46, 02-668 Warszawa, Poland

The rotational spectrum of methylene iodide, CH_2I_2, has hitherto resisted assignment owing to a combination of the large double iodine nuclear quadrupole coupling, small rotational constants, and low frequency ICI bending vibrational mode. We have independently attempted in Bologna and Warsaw to make progress through the analysis of the higher-J mm-wave transitions which were expected to have more compact splitting patterns. It was however only when we combined the capabilities of our respective spectrometers that the spectrum was solved.

The supersonic molecular jet mm-wave spectrometer in Bologna allowed selection and unambiguous assignment of 15 ground state transitions in the 70 GHz region. The approximate centre frequencies derived by averaging over the clearly visible complete nuclear quadrupole patterns then made possible the assignment of the broad-band spectra up to 330 GHz, which were recorded earlier on the BWO spectrometer in Warsaw. The assignment was greatly aided by using starting values for the quartic centrifugal distortion constants calculated from the *ab initio* force field. The final fit is based on over 150 rotational transitions with values of J ranging up to 170 and accurate values for the quadratic, quartic and some sextic constants were obtained. Nuclear quadrupole structure for some transitions was fitted and initial values for splitting constants are reported. Partial assignment of rotational transitions in the vibrational satellite progression associated with the ICI bend has also been made. The structure of CH_2I_2 resulting from the rotational and hyperfine splitting constants is discussed.

M28

INFRARED ABSORPTION CROSS SECTIONS AND BAND
STRENGTHS OF HFC-32 VAPOUR (DIFLUOROMETHANE)

G. Duxbury[a], K. Smith[a],

D Newnham[b], M. Page[b] and J Ballard[b]

[a]Department of Physics and Applied Physics, University of

Strathclyde, J. A. Bldg., 107 Rottenrow, Glasgow G4 0NG, Scotland.

[b]Space Science Department, Rutherford Appleton Laboratory,

Chilton, DIDCOT, Oxfordshire, OX11 0QX, U.K.

Recent legislation controlling the use of Chlorofluorocarbons (CFCs) has led to the introduction of replacement chemicals, Hydrochlorofluorocarbons (HCFCs), in a wide range of domestic and industrial applications. However, from 2030 the usage of HCFCs themselves becomes controlled and they are to be replaced by more environmentally acceptable Hydrofluorocarbons (HFCs).

The C-H bond present in HCFCs and HFCs allows destruction in the atmosphere by reaction with OH radicals, significantly reducing their lifetime compared with CFCs. However, HCFC and HFC compounds absorb mid- infrared radiation strongly in the 8-12 μm atmospheric window region. It is therefore important to include data on these absorptions in radiative transfer calculations used to model warming of the Earth's atmosphere.

Medium resolution (0.03 cm-1) Fourier transform infrared spectroscopy was used to determine absorbance cross-sections and integrated band strengths of the ν_3, ν_5, ν_7, ν_8 and ν_9 bands of HFC-32 (difluoromethane) vapour at six temperatures (203, 213, 233, 253, 273 and 294 K). In addition air-broadened spectra have been recorded at three temperatures (203, 253 and 294 K) using mixtures containing 5, 20 and 100 kPa of dry air.

To allow ro-vibrational analysis high resolution (0.0015 cm-1) spectra were obtained of the ν_1, ν_3, ν_5, ν_6, ν_8 and ν_9 bands of HFC-32 at 203 and 294 K.

M29

ROTATIONAL SPECTRUM AND INTERNAL ROTATION BARRIER OF 1-CHLORO-1-FLUOROETHANE[1]

R. Hinze*†, A. Lesarri*, J. C. López*, J. L. Alonso*

and A. Guarnieri†

*Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain, and

†Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

The rotational spectrum of 1-chloro-1-fluoroethane has been analysed in the frequency region 8-250 GHz. Accurate rotational, centrifugal distortion and quadrupole coupling constants have been determined for the ground state of the ^{35}Cl and ^{37}Cl isotopomers. The spectra of the two lowest vibrational excited states have been also investigated. FT-MW experiments carried out in the frequency region 8-18 GHz show that the strongest satellite lines are splitted by internal rotation of the methyl group. This is an evidence that this satellite must be assigned to the first excited state of the methyl torsion vibration in disagreement with the previous assignment of this satellite to a bending motion[2]. The barrier to internal rotation of the methyl group has been determined from these splittings to be 3876 ± 10 cal mol^{-1}. This value is in good agreement with the predictions of ab initio calculations

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M30

The Microwave Spectra of some Unstable Molecules Prepared Using a Pulsed Electric Discharge

Bethany Gatehouse, Holger S.P. Müller, and Michael C.L. Gerry

Department of Chemistry, University of British Columbia,
2036 Main Mall, Vancouver, B.C., Canada, V6T 1Z1

An electric discharge system has been constructed for use in generating free radicals and other unstable species in a pulsed jet for microwave spectroscopic study. This apparatus consists of a nozzle cap containing two concentric brass disc electrodes, separated by a spark gap of 2 mm, which is mounted in front of a General Valve series 9 pulsed nozzle. Pulsed voltages of roughly 5 or 10 kV can be applied.

The nozzle system was tested by preparing such unstable species as SF_2, FBO, ClBO, FBS and ClBS; their spectra were measured using a cavity pulsed microwave Fourier transform spectrometer. The resolution of this instrument is such that hyperfine structure in these transitions due to quadrupole, spin-rotation, and spin-spin interactions was resolved. For SF_2, ^{19}F spin-rotation and spin-spin coupling constants were measured, and, in the XBE species, quadrupole splittings due to the boron nucleus, as well as spin-rotation and spin-spin coupling effects, were measured; all for the first time. The determined hyperfine coupling constants are interpreted in terms of the molecular structures.

Microwave Spectrum and Structural Analysis of the Dimer of Pyrrole

Gieri Columberg and Alfred Bauder

Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland

The rotational spectrum of the dimer of pyrrole has been measured between 8 and 18 GHz using a pulsed nozzle Fourier transform microwave spectrometer. In addition to the parent species, nine ^{15}N and D isotopomers have been analysed. Rotational constants, centrifugal distortion constants and, for two isotopomers, ^{14}N quadrupole coupling constants have been fitted to the measured frequencies of rotational transitions. The observed rotational constants are consistent with a T-shaped structure for the dimer. The planes of the two pyrrole molecules are approximately perpendicular with the nitrogen side of one ring directed to the π electronic system of the other ring forming a hydrogen bond. From the rotational constants of six isotopomers a partial structure of the dimer has been determined. Three structural parameters have been fitted to the differences between the planar moments of the isotopically substituted species and the parent species. The centrifugal distortion constants of the dimer of pyrrole-^{15}N have been used to determine the frequency of the van der Waals stretching mode and the dissociation energy of the complex in a pseudo-diatomic approximation.

M32

PRESSURE BROADENING
IN THE $^{13}C^{16}O$ 2-0 BAND

S. Dreher, S. Voigt, J. Orphal and J.P. Burrows

Institute of Environmental Physics, University of Bremen

P.O. Box 33 04 40, D-28334 Bremen, Germany

e-mail: dreher@gome3.physik.uni-bremen.de

Air broadening of rotation-vibration lines of the $^{13}C^{16}O$ 2-0 band centered at 4167 cm^{-1} was investigated using our newly-installed Fourier Transform Spectrometer BRUKER IFS 120 HR. The instrument can be operated in the 2000 - 45000 cm^{-1} range. Spectra can be obtained either from one-sided or from double-sided interferograms. A maximum spectral resolution of 0.0042 cm^{-1} can be achieved.

For the studied wavenumber range we used a combination of a tungsten lamp and a liquid nitrogen cooled InSb detector. A sample of 99 % isotopically pure $^{13}C^{16}O$ was provided by the Cambridge Isotope Laboratories (Massachusetts, USA). The spectra were recorded at room temperature placing the CO-air mixture in a White-type long path cell where the optical path length can be varied between 2 and 40 meters.

M33

"SOFT" AND "HARD" COLLISION MODELS. EXPERIMENTAL OBSERVATION OF DIFFERENCE IN SPECTRAL LINE SHAPE

Alexander Nadezhdinskii

General Physics Institute, Russian Academy of
Sciences, Moscow, Russia

ABSTRACT

Voigt profile fitting routine was used to obtained all parameters
of spectral line under investigation, such as transition frequency,
line intensity, Lorentzian and Gaussian parameters of time shape.
The routine was used to fit computer simulated "soft" and
"hard" profiles with different narrowing and broadening
parameters. Simultaneously several results were obtained in
analytical form and were compared with computer modeling
showing approach validity.

Small, but observable difference between models under
consideration was observed for pressure dependence of Gaussian
parameter. Comparison between experimental results obtained
for water self-broadening in 1.9 microns region and different
models showed validity of "soft" collisional model in this case.
The physical explanation of the last result is pole of scattering
probability at zero angles for dipole-dipole interaction.

Present results explain un-physical values of collisional
narrowing parameters obtained previously in similar
investigations. As a result of present work, ro-vibration state
dependence of partial translation cross-section can be determined
for different molecules.

M34

SELF-BROADENING COEFFICIENTS FROM
FTIR MEASUREMENTS OF H_2O

K. A. KEPPLER, G. Ch. MELLAU, S. KLEE, Vl. G. TYUTEREV,
S. N. MIKHAILENKO, B. P. WINNEWISSER, M. WINNEWISSER
and K. NARAHARI RAO

Self-broadening parameters have been extracted for selected transitions
observed in the spectrum of water between 1860–6600 cm^{-1}. The spec-
trum of water at room temperature in natural isotopic abundance has
been recorded in this region at pressure–broadening–limited resolution
with a Bruker FTS 120HR and a White–type cell adjusted to provide
pathlengths of 64–288m. Sample pressures used were 0.005–31.3mbar.
The results of the broadening determinations will be presented and dis-
cussed.

Address of Keppler and Rao: Department of Physics, The Ohio State
University, Columbus, OH, USA 43210–1106.

Address of Klee, Mellau, Winnewisser, and Winnewisser:
Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen,
D-35392 Giessen, Germany.

Address of Tyuterev: GSMA Laboratoire de Physique Moleculaire et
Atmospherique, URA CNRS D 1434, Faculte des Sciences Universite
de Reims, BP 347-51062 REIMS Cedex France.

Address of Mikhailenko: Institute of Atmospheric Optics, 634055,
Tomsk, Russia.

M35

COLLISIONAL RELAXATION OF THE ν_2 BAND OF HCN
INVESTIGATED WITH A FREQUENCY STABILIZED DIODE LASER

A. BABAY, V. LEMAIRE, B. LEMOINE, F. ROHART

Laboratoire de Spectroscopie Hertzienne, URA 249,
BAT P5, Cité Scientifique, 59655 Villeneuve d'Ascq Cedex

The relaxation of the ν_2 band of HCN, a minor species of Titan, Saturne and Jupiter atmospheres has been investigated.

The measurements were performed using a stabilized tunable diode laser spectrometer. Its spectral performances have been carefully studied in order to get a reliable apparatus function. The consequences on line intensities and broadenings will be presented.

Broadening of high J values have been measured using H_2, Ar and HCN as buffer gases. They are in good agreement with measurements previously published for other vibrational bands.

These results have been interpreted in collaboration with J.P. Bouanich from the "Laboratoire de Physique Moléculaire et Application" (Orsay, France) with the semi-classical formalism of Robert and Bonamy, using suitable collisional interaction potentials.

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M36

WHAT HAPPENS IN FTS WHEN THE EXPERIMENTAL CONDITIONS VARY DURING THE RECORDING TIME?

V. Dana, J.-Y. Mandin, and M.-Y. Allout

Laboratoire de Physique Moléculaire et Applications

Unité propre du CNRS, associée aux Universités Paris VI et Paris XI

Université Pierre et Marie Curie, Tour 13, case 76

4, place Jussieu, 75252 Paris Cedex 05, France

For step by step as well as for rapid scan interferometers, the recording usually requires several hours in high resolution laboratory experiments, and it is often difficult to have stable experimental conditions (such as pressure and temperature) for so long durations, especially when unstable species (*e.g.*, $HNO_3, O_3 ...$), or molecules having strong adsorption (*e.g.*, AsH_3), are concerned.

In this communication, we discuss the effects of a variation of the pressure of the absorbing gas on the retrieved line intensities and collisional widths. Various cases are presented for the two types of interferometers: linear and exponential variation of this pressure, for gaussian, Voigt, and lorentzian line shapes, and with different ratios of increasing or decreasing of the pressure. Two situations have been considered: the absorbing gas is alone in the cell or mixed with other gases whose partial pressures can also vary during the recording. In this last case, the decomposition of the absorbing gas has been studied.

A similar study concerning the variation of the temperature is in progress.

M37

THE INFRARED SPECTRUM OF THE
VAN DER WAALS COMPLEX (CO)$_2$

M. Havenith, S. König, G. Hilpert, C. Lubina,
M. Scherer, H. Linnartz, M. Petri
Institut für Angewandte Physik, Wegelerstr. 8,
53115 Bonn, Germany

By means of diode laser spectroscopy we were able to observe signals of
(CO)$_2$ in a supersonic jet expansion. The transitions were detected using
frequency modulation and concentration-frequency double modulation. The
concentration-frequency double modulation technique was recently developed
in our group [1,2] and combines a 50% duty cycle with high repetition rates
(3-8 kHz).
These measurements yield the first analyzed spectra of (CO)$_2$ and give for the
first time access to the spectroscopic parameters of this dimer. The analysis
is complicated by the high density of lines. We will show the result of a
preliminary fit. The intensity in the observed subbands resembles a free rotor.
These measurements can be considered as the first step towards an
understanding of this molecular complex.

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M38

Pure rotational spectrum of HF in Ar gas: line parameters and line profiles.

I. M. Grigoriev, N. N. Filippov, V. V. Milevski, and M. V. Tonkov
Institute of Physics, St.Petersburg University,
Peterhof, 198904 St.Petersburg, Russia

J. Boissoles, G. Monnier, and B. Khalil
Département de Physique Atomique et Moléculaire, URA 1203 du CNRS,
Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France

The far-infrared absorption spectrum of gaseous hydrogen fluoride mixed with argon was investigated under the variation of pressure from 1 to 400 bar at room temperature. We performed the lower pressure measurements (1–30 bar) with the BRUKER IFS 120 HR spectrometer (Rennes) and the higher pressure measurements (30–400 bar) with the LFS–1000 Fourier transform spectrometer (St.Petersburg). In both cases the measurements were made under the optimal transmission conditions without instrumental broadening. The non-linear fit for linewidth and lineshift density dependences was tested, the deviations from linearity, however, were found to be within experimental errors. The line asymmetry for higher pressures was detected. For the lines $R(0) - R(10)$ width and shift cross-sections were determined.

The comparison of the experimental width and shift cross-sections with the most recent close-coupling calculations[1] reveals their accordance for lower J values. For higher J the measured broadening coefficients are slightly greater than the calculated ones whereas the lineshifts demonstrate non-zero J asymptotic behavior contrary to the theoretical prediction.

We compare the lineshape parameters with those obtained recently (St.Petersburg) for the mixtures of HF with He and Xe. The measured width cross-sections are intermediate between those for He and Xe. For shifts the J dependence in the case of Ar is close to that for Xe including the asymptotic behavior. The rotational cross-sections are less than those for vibration-rotation spectrum.

The line asymmetry found at elevated pressures (30–400 bar) when the lines overlap significantly is interpreted qualitatively as the evidence of the line mixing effect. The corresponding asymmetry parameters calculated within the framework of the impact semiclassical approach[2] are close to the measured ones.

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M39

SUBDOPPLER SPECTROSCOPY WITH A TUNABLE SIDEBAND SPECTROMETER: WHAT'S NEW?

E. Rusinek, M. Khelkhal, F. Herlemont and J. Legrand

Laboratoire de Spectroscopie Hertzienne U.R.A. 249

Université des Sciences et Technologies de Lille

59655 Villeneuve d'Ascq Cedex France

A tunable sideband spectrometer has been developped in Lille to perform subDoppler spectroscopy. It is based on a CO_2 laser which is frequency locked on CO_2 saturation resonance and makes use of two electrooptic modulators working in the 0-4 GHz range and in the 8-18 GHz. These two modulators can be use to perform saturation spectroscopy or infrared-infrared double resonance. The resolution is better than 100 kHz (H.W.H.M.) and absolute frequency accuracy up to 10 kHz. Spectra of SF_6, C_2H_4, and CDF_3 will be shown to illustrate both the tunability and the resolution of the spectrometer.

M40

Amplification of atomic fields by stimulated emission of atoms

Christian J. Bordé

Laboratoire de Physique des Lasers,
URA du CNRS 282,
Université Paris-Nord, Villetaneuse, France
and
Laboratoire de Gravitation et Cosmologie Relativistes,
URA du CNRS 769,
Université Pierre et Marie Curie, Paris, France

May 31, 1995

A new way towards the achievement of a coherent source of atoms ("atom laser" or "atomaser" or "ataser") is explored. We discuss the possibility to amplify matter-waves by stimulated emission of massive bosons. More specifically, we consider the example of induced dissociation of molecules under the influence of an incident atomic wave and compare it to the special case of the induced emission of ground state atoms from excited atoms. General formulas for the gain and for the spontaneous dissociation rate, which apply to both cases, are derived from Relativistic Quantum Field Theory. Several realistic possibilities including controlled dissociation of electronically excited dimers or of vibrationally excited Van der Waals molecules and various dissociative recombination schemes are discussed.

M41

CO$_2$ Faraday LMR Spectroscopy of Ro-vibrational Transitions of SiC

M. Wienkoop, P.-C. Schumann, P. Mürtz and W. Urban
Institut für Angewandte Physik der Universität Bonn
Wegelerstraße 8, D-53115 Bonn, Germany

We report the first observation of the SiC molecule detected in the spectral region around 950 cm^{-1}. The measurements were performed with the Faraday laser magnetic resonance (LMR) spectrometer utilizing a CO$_2$-Laser.

With this high-sensitive technique we observed several weak lines which we assigned to the v=1←0 transition in the ground state X'Π_2. The SiC was produced in a gas phase reaction between SiCl$_4$ and CO by means of an electric DC glow discharge of normal type.

Due to the low signal intensities the spectroscopy of infrared transitions turned out to be very difficult. From earlier measurements of electronic transitions the production of SiC is known to be very difficult. Moreover, the calculation of transition moments shows, that infrared transitions are weak. In order to increase the signal-to-noise ratio we investigated different production methods and improved the sensitivity of our spectrometer. The recent results are presented on this poster.

M42

FAST COMPUTER CODES BASED ON LINE-BY-LINE METHOD FOR APPLICATION IN ATMOSPHERIC OPTICS.

K.M.Firsov, M.Yu.Kataev, A.A.Mitsel,

Yu.N.Ponomarev, I.V.Ptashnik.

Institute of Atmospheric Optics,

1, Akademicheskii Ave., 634055, Tomsk, Russia

A number of computer codes are created to perform: the calculation the atmospheric absorption by line-by-line method; the simulation of the optical beam propagation through the atmosphere and the laser sounding of the atmospheric gases. A computer code also is applied for creation of the parametric models of transmittance based on the K-function method.

The version of the fast line-by-line method is described. To decrease the time of computation we use: new line selection criterion enabling one to reduce the number of lines with the altitude increasing; non-uniform wavenumber grid for absorption coefficient that grows with increase of the frequency detuning from the center of line; independent calculation of the selective and continuum absorption.

The description of the parametric model of transmittance is presented. This model enables us to calculate the extinction of optical radiation with high accuracy. The effective way to determine expansion parameters is based on line-by-line method with using orthogonal exponential functions. The rigorous solution of the overlapping band problem is obtained with use of Laplase transformation.

M43

ASSIGNMENT OF HOT METHANE LINES IN COMET SHOEMAKER-LEVY 9 COLLISION SPECTRA

B.M. Dinelli (ISM CNR - Bologna, Italy and University College London, U.K.), S. Miller, N. Achilleos, and J. Tennyson (University College London, U.K.), M.-F. Jagod and T.Oka (The University of Chicago, U.S.A.), J.C. Hilico (Université de Bourgogne - Dijon, France), T.R. Geballe (UKIRT, Hawaii, U.S.A.)

On July 17, 1994, the effects of the impact of Fragment C of Comet Shoemaker-Levy 9 with Jupiter were monitored at a wavelength of 3.5 μm using the CGS4 spectrometer in echelle mode ($\frac{\lambda}{\Delta\lambda} = 15000$) of the UKIRT telescope at Mauna Kea (Hawaii). All the spectra were taken with the slit along the 44°S latitude of Jupiter, the latitude at which the impacts occurred.

Before the impact the spectra showed H_3^+ emission lines typical of the quiescent ionosphere. About 6 minutes after the impact, the Jupiter spectrum showed an enormous brightening (of about a factor of 40) of the rows containing and adjacent to the east (impact) limb of the planet. The spectrum showed very intense multiplets superimposed on a very strong continuum. Using the HITRAN list of methane lines we could assign the strongest multiplets in our spectra as CH_4 ν_3 lines - P(18) and P(19) multiplets(1). These appeared to be sitting on a continuum baseline generated by a black body source at the core of the explosion. There were also a number of unassigned lines. Using the new analysis of the pentad system of methane of Hilico et al.(2), however , most of these were assigned to methane hot bands, in particular to the P branch of $\nu_3 + \nu_4 \leftarrow \nu_4$ hot band of methane. Moreover the baseline of our spectra was reproduced by a 'grass' of weak hot bands and overtone bands transitions of methane.

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N1

THEORETICAL LONG-RANGE POTENTIAL ENERGY CURVES FOR DIATOMIC MOLECULES. APPLICATIONS TO VARIOUS STATES OF ALKALI DIMERS.

G. Hadinger, S. Magnier and M. Aubert-Frécon

Laboratoire de Spectrométrie Ionique et Moléculaire

CNRS et Université Lyon I, 69622 Villeurbanne Cedex, France

There is an increasing interest nowadays for accurate predictions of long-range potential energy curves for ground and excited molecular states of diatomic systems, in particular of alkali dimers, connected with the topic of cold atoms. In the range of R, typically longer than $\approx 30\ a_0$, specific models are more suitable and by far less expensive than ab initio methods which are well adapted to shorter distances. The model we propose is based on a multipolar expansion of the coulombic interaction energy corrected or no corrected for overlap effects and on an estimation of the exchange interaction energy by a surface integral method. If the pertubative approach of the long-range coulombic interaction is conceptually well known, the surface integral method (in its asymptotic form) is not as yet popular. So some details about this approach and some useful analytical results will be presented, together with long-range expansion coefficients C_n (re-) calculated on accurate model potential basis sets.

Concrete applications for the states $X\,^1\Sigma_g^+$ of K_2, 1g $((1)\,^1\Pi_g)$ of Rb_2 and $O_u^+\,((1)^1\Sigma_u^+)$ of Li_2 will be presented and discussed in tight connection with recent experimental spectroscopic results for these states at long-range $(\approx 200\ a_0)$.

N2

FTIR-spectroscopy applied in the study of gas phase reaction kinetics using isotopes.

Jonas Blomquist, Katja Duncan, Niels Wessel Larsen,

Flemming M. Nicolaisen and Thorvald Pedersen.

Laboratory of Molecular Spectroscopy

Institute of Chemistry, University of Copenhagen.

The H. C. Ørsted Institute, Universitetsparken 5

DK-2100 Copenhagen Ø, Denmark

and Jens Sehested

Risø, Roskilde, Denmark

High resolution FTIR spectroscopy has been used in the investigation of two different gas phase exchange reactions. In both cases ^{18}O (denoted Q below) was used in the reactions, thus making it possible to measure the extent of reaction spectroscopically:

i) The exchange reaction between carbondioxide and ^1D oxygen atoms:

$$CO_2 + Q(^1D) \rightarrow OCQ + O \qquad (1)$$
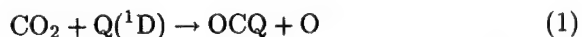
The reaction was performed by repeated UV photolysis of a mixture of Q_3 and $^{13}CO_2$, and FTIR was used to monitor the concentrations of Q_3 and $O^{13}CQ$.

ii) The exchange reaction between OH radicals and oxygen molecules:

$$OH + Q_2 \rightarrow QH + OQ \qquad (2)$$

This reaction was initiated by pulse radiolysis of a mixture of SF_6, H_2O, Q_2 and butane. If the exchange reaction takes plase then H_2Q will be formed. The resulting Q enrichment of water was measured by FTIR spectroscopy.

SCATTERING APPROACH TO THE CALCULATION OF EXCITED STATES OF CaF AND BaF

M.ARIF and Ch.JUNGEN

Laboratoire Aimé Cotton

Université Paris-Sud

91405 Orsay France

The entire electronic level spectrum and wave functions of the dipolar molecules CaF and BaF are derived from properties of the constituent atoms alone, namely the quantum defects of the Ca^+ and Ba^+ metal ions as well as the polarisabilities of Ca^{++}, Ba^{++}[1] and F^- [2].

The motion of the lone molecular valence electron is treated as a double scattering process involving the closed-shell metal ion M^{++} and cation X^- centers, whereby the negative ion X^- is regarded as a point charge[3].

All known electronic states of CaF and BaF extending up to the principal quantum number n=15 are well reproduced by the calculations.

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N4

HIGH RESOLUTION FOURIER SPECTROMETRY OF THE $^{14}N_2^+$ ION FOR OPTICAL DIAGNOSTICS IN AIR PLASMA

Françoise MICHAUD and Françoise ROUX
Laboratoire de Spectrométrie Ionique et Moléculaire
Université Claude Bernard Lyon I, 43 Bd du 11 Novembre 1918
69622 Villeurbanne Cedex, France

Sumner P. DAVIS and An-Dien NGUYEN
Department of Physics, University of California,
Berkeley, California 94720

Christophe O. LAUX
High Temperature Gasdynamics Laboratory,
Stanford University, Stanford, California 94305

Optical diagnostics and radiative modeling require accurate spectroscopic data to predict the radiation of air observed in the re-entry of spaces vehicles in the earth's atmosphere. A comparison between the experimental spectrum and a numerical simulation (Code NEQAIR) shows important disagreements when the perturbations are not modeled.

The aim of the present work is to carry out a more complete deperturbation of the strongly perturbed N_2^+ *first negative system* $B\ ^2\Sigma_u^+ \rightarrow X\ ^2\Sigma_g^+$.. This analysis is performed based on spectra excited at low and high temperature in a hollow cathode and in a Pointolite lamp (high J values up to 95 are observed in the O$\rightarrow$ v" bands). Deperturbed constants and interaction parameters describing the $B\ ^2\Sigma_u^+ \sim A\ ^2\Pi_u$ perturbation are derived. The standard deviation of the fit is $\sim 10 \times 10^{-3}\,cm^{-1}$.

The predictions of NEQAIR 2 which use the results of the deperturbation are found to be in excellent agreement with experimental spectrum observed in a plasma torch over the range 4500 - 7500 K.

N5

STUDY OF PERTURBATIONS OBSERVED IN THE RYDBERG
$C^1\Sigma^+$ AND E $^1\Pi \to$ B $^1\Sigma^+$ SYSTEMS OF CO

André LE FLOCH[1] and Claude AMIOT[2]

(1) Département de Physique, Université de Tours, F-37200, and DAMAP,

URA 812, Observatoire de Paris-Meudon, F-92195.

(2) Laboratoire Aimé Cotton, CNRS II, Orsay, F-91405

Perturbations previously observed by Amiot et al [1] from high resolution FTS in the Rydberg $C^1\Sigma^+ \to B^1\Sigma^+$ and E $^1\Pi \to B^1\Sigma^+$ systems of $^{12}C^{16}O$ and $^{14}C^{16}O$ are studied.

It is shown that all these perturbations can be interpreted from:

(1) Interactions between the Rydberg $B^1\Sigma^+$ (v=0) state, and upper vibrational levels of the valence $e^3\Sigma^-$ and $A^1\Pi$ states;

(2) Interactions between the Rydberg $C^1\Sigma^+$ (v=0) and $E^1\Pi$ (v=0) states, and the valence $k^3\Pi$ (v=1 - 4) state recently discovered by Baker and Launay [2].

A simultaneous numerical treatment of wavenumbers of the C → B and E → B systems, including these interactions, is also performed for each isotopomer.

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N6

SPECTROSCOPICALLY DETERMINED BORN-OPPENHEIMER AND ADIABATIC SURFACES FOR H_3^+

BIANCA M. DINELLI[a], OLEG L. POLYANSKY[b] AND JONATHAN TENNYSON

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom.

[a] Permanent Address: Istituto di Spettroscopia Molecolare, Bologna, Italy
[b] Present address: Physical-Chemistry Institute, Justus-Liebig-University, Giessen,Germany

Despite the accuracy of *ab initio* calculations for H_3^+, they still show systematic, and by spectroscopic standards, large errors. We have therefore been using the extensive spectroscopic data to determine potential energy surfaces for this system.

Initially, fits were performed to 243 'observed' H_3^+ energy levels with rotational level, $J \leq 9$. These calculations used the program TRIATOM and reproduced the data with a standard deviation of 0.053 cm^{-1} [1]. However the resulting potential was found to perform poorly for deuterated isotopomers; this behaviour was ascribed to failure of the Born-Oppenheimer (BO) approximation.

Using fits to both H_3^+ and D_3^+ data it was demonstrated that both a BO potential and the leading non-BO term, the adiabatic correction, could be obtained [2]. However the lack of experimental data and, in particular, its unevenness between the isotopomers meant that full surfaces could not be determined in this fashion. The adiabatic correction was therefore determined *ab initio* for both the symmetric isotopomers, H_3^+ and D_3^+ [3] and asymmetric isotopomers, H_2D^+ and D_2H^+ [4].

Starting from these surfaces and using new data for D_3^+, we have performed simultaneous fits of the BO potential, symmetric and asymmetric adiabatic corrections to spectroscopic data for all 4 isotopomers. This fit reproduces all the data to ~ 0.015 cm^{-1}, close to the underlying experimental accuracy. However there is some evidence from the behaviour of higher rotational levels that these are sensitive to non-adiabatic effects.

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THE $X^1A_{1g}0_0$ and $A^1B_{2u}6^1$ ELECTRONIC STATE POLARIZABILITIES OF FREE BENZENE MOLECULES

M. Okruss, R. Müller and A. Hese

Institut für Strahlungs- und Kernpyhsik
Technische Universität Berlin
Hardenbergstr. 36, D-10623 Berlin

We report on the first measurements of both ground ($X^1A_{1g}0_0$) and excited ($A^1B_{2u}6^1$) electronic state polarizabilities of free benzene molecules by means of Laser Stark Spectroscopy in extremely high electric fields. A jet of free and rotational-cooled benzene molecules was crossed perpendicularly by a narrow-band tunable cw UV-laser. A capacitor generated an electrostatic field with field strengths of up to 250 kV/cm in the interaction region. Despite the extreme field strength resulting line shifts in the 6_0^1-band of the $S_1 \leftarrow S_0$ transition at 38606 cm^{-1} were only of the order of the linewidth (30 MHz). The frequency shifts of individual rotational transitions yield the ground and excited state polarizabilities by using second order perturbation theory:

polarizability in a.u.	ground state S_0, vibrationless	exc. state S_1, 6^1
in the molecular plane [1] $P_{aa} = P_{bb}$	79.2	82.6(9)
perpendicular to the molecular plane P_{cc}	50.6(9)	63.1(9)

In the observed spectral range ($\approx$ 100 lines) one rotational line shows unexpected large Stark-effect. Possibly, this behaviour is caused by an unknown perturbation of this band

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THE ELECTRIC DIPOLE MOMENTS IN THE VIBRATIONLESS X¹A' AND A¹A' STATE OF 2-FLUORONAPHTHALENE

I. Rückert, M. Okruss and A. Hese

Institut für Strahlungs- und Kernpyhsik
Technische Universität Berlin
Hardenbergstr. 36, D-10623 Berlin

We apply high resolution Laser Stark spectroscopy to determine the permanent electric dipole moments of aromatic molecules in different electronic states. After the method was successfully tested at 1-fluoronaphthalene [1], 2-fluoronaphthalene (2FN) was chosen to investigate the influence of the fluorine substitution position. The $S_1(A^1A') \leftarrow S_0(X^1A')(0^0_0)$ band spectrum was recorded at 314.4 nm, for the first time rotationally resolved, using a 2FN seeded supersonic argon beam and a frequency doubled ring dye-laser system. About 400 lines were included in a least squares fit of the rotational constants leading to an estimated standard deviation of the calculated line frequencies of 2 MHz. The hybrid character of the band was found to be 90% b-type and 10% a-type. The fit results for the dipole moments in the molecule-fixed axis system are:

X^1A'-state: $\mu_a = 1.556(13)D$ $\mu_b = 0.580(6)D$ $|\vec{\mu}| = 1.660(14)$ D
A^1A'-state: $\mu_a = 1.459(12)$ $\mu_b = 0.487(5)$ $|\vec{\mu}| = 1.538(13)$

Additionally, an electric field strength of the order of 150 kV/cm was applied to study the behaviour of the molecule in an extreme electric field.

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N9

F.T. SPECTROSCOPY OF OCS FROM 3700 TO 4800 CM^{-1}
(SELECTION OF A LINE POINTING PROGRAMME)

S. Naim and A. Fayt

Molecular spectroscopy laboratory - Université Catholique de Louvain

2 Chemin du Cyclotron - B-1348 Louvain-La-Neuve

I. Dubois and H. Bredohl

Institut d'Astrophysique - Université de Liège

5 avenue de Cointe - B-4000 Liège

F.T. spectra of carbonyl sulfide (OCS) have been recorded in Liège from 3700 to 4800 cm^{-1} with a resolution of 0.007 cm^{-1}. More than 120 bands have been identified and assigned to different isotopometers, thanks to predictions of frequencies and intensities based on our previous analyses of this molecule.

The new data have been introduced in the global analyses of the different isotopometers which take into account l-type and anharmonic resonances in a one-step diagonalization procedure. All data are fitted in agreement with experimental uncertainties.

The analysis of experimental intensities has shown special J-dependences of intensities due to the anharmonic resonances. They are well reproduced by taking into account the mixing of the states on the basis of their eigenvectors determined from the frequency analysis.

QUALITATIVE TREATMENT OF THE FIRST TRIAD
OF VIBRATIONAL STATES OF THE H_2O MOLECULE

A.V.BURENIN

Institute of Applied Physics, Russian Academy of Sciences,
46 Uljanov Street, 603600 Nizhny Novgorod, Russia

The most simple treatment of the first triad of the vibrational states of the H_2O molecule is suggested using the assumption that the observed vibrational quasi-degeneracy is not accidental, but is due to the existence of a wider symmetry group than the point group of the molecule for the main contribution to the considered intramolecular motion. Such idea of treating a family vibrational states of a rigid molecule coupled with accidental resonances has been suggested in [1]. If only the main contribution is taken into account, all the family is reduced to one degenerate vibrational state that can conveniently be characterized by the vibrational spin operator. The latter is a specific case of the coordinate spin operator of the molecule [2]. The use of the coordinate spin in the frames of the approach to analyzing the symmetry properties of the intramolecular motion based on the concept of a chain of symmetry groups [3] enables one to solve rather easily a very complicated problem of determining a complete expression in the form of the Taylor series in dynamic variables for the effective operator of any physical value characterizing the molecule with account of vibrational quasi-degeneracy. Obvious advantages of this treatment of the family of coupled vibrational states are: 1) the operational formulation for both the rotational and vibrational types of motion (the corresponding dynamic variables are the total angular momentum operator and the coordinate spin operator); 2) automatic consideration of all possible resonance types in an arbitrary order of the perturbation theory; 3) essentially simplified solution of the reduction problem. Some new results have been obtained on both the treatment of the first triad of vibrational states of the H_2O molecule and on further development of the employed method.

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Five-dimensional local mode-Fermi resonance model for overtone spectra of ammonia

Esa Kauppi and Lauri Halonen

Laboratory of Physical Chemistry, P. O. Box 55 (A. I. Virtasen aukio 1),
FIN-00014 University of Helsinki, Finland

A five-dimensional vibrational Hamiltonian in terms of curviliner internal valence coordinates has been constructed to model overtone spectra of the ammonia molecule. The model Hamiltonian includes the three stretching vibrations and the doubly degenerate bending vibration. In the first approximation, the symmetric bending vibration coordinate is constrained into its equilibrium value. Thus the model is useful for vibrational energy levels with the symmetric bending vibration, which is associated with the inversion motion, on its ground state. The kinetic energy operator in the model Hamiltonian is obtained by expanding the elements of the Wilson's **G** matrix as Taylor series. The NH stretching vibrations are described by a local mode Hamiltonian with three bilinearly coupled anharmonic bond oscillators. In the zeroth-order, the doubly degenerate bending vibrations are described by a two-dimensional isotropic Harmonic oscillator in the cartesian representation. Cubic and quartic anharmonic bending terms are also included. The most important coupling terms between the stretching and bending degrees of freedom are the Fermi resonance terms. The potential energy function is expanded as Taylor series in terms of the curvilinear internal valence coordinates leading to isotope invariant model potential energy function. Vibrational energy levels have been calculated using Van Vleck perturbation theory. Non-linear least squares method has been employed to optimise the potential energy parameters using observed vibrational band origins as data. Amounting altogether 34 vibrational band origins observed for $^{14}NH_3$, $^{14}ND_3$, and $^{14}NT_3$ isotopomers have been reproduced within a standard deviation of 5.5 cm^{-1} using one set of isotope invariant potential energy parameters. The optimised potential energy surface compare well with results of *ab initio* electronic structure calculations. Vibrational states have been labelled using local mode-Fermi resonance quantum numbers based on the leading contributions in the eigenvectors obtained. However, Fermi resonance interactions are strong in several vibrational polyads, which makes the quantum number labels for many individual levels insignificant.

THE $2v_1+2v_3$ BAND OF OZONE

A. Barbe and J.J. Plateaux

G.S.M.A., U.A. CNRS D 1434

Faculté des Sciences

BP 347 - 51062 REIMS Cédex - France

The $2v_1+2v_3$ band of ozone, appearing in the 4150 cm^{-1} region has been observed for the first time, using high resolution Reims FTS and large product p * ℓ of 3616 cm * 48 Torr. 259 transitions have been assigned, involving J and Ka up to 55 and 9 respectively. The fit on the 180 corresponding energy levels using single Watson type hamiltonian leads to a standard deviation of 1.3 10^{-3} cm^{-1}, of the order of experimental accuracy. The line intensities are also measured and calculated with suitable transition moment operators. The set of parameters, transition moment operators, as well as comparisons between observed and calculated wavenumbers and intensities are presented.

N13

THE v_4 BAND OF NH$_3^+$

Frank Kühnemann[a], Sangwoo Joo and Takeshi Oka

Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL. 60637, USA

Rafael Escribano

Instituto de Estructura de la Materia, C.S.I.C., Serrano 119, 28006 Madrid, Spain

a) present address: Institut für Angewandte Physik , der Universität Bonn, Wegelerstrasse 8, 53115 Bonn, Germany

The v_4 degenerate band of the ammonia cation NH$_3^+$ has been observed using tunable diode lasers combined with the velocity modulation technique. NH$_3^+$ is produced in air or liquid nitrogen-cooled ac glow discharges of N$_2$, H$_2$ and He. This ion has already been the subject of previous works in this lab[1,2]. Spin-rotation doublets are observed and interpreted on some of the transitions. The spectrum is assigned and vibration-rotation constants are derived for the $v_4=1$ state. The effect of the Coriolis perturbation with the $v_2=1$ state, situated more than 400 cm^{-1} below, is discussed.

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The Rovibrational Spectrum of BrCN. A Combined High Resolution Infrared and Millimeterwave Study.

M. Le Guennec
Laboratoire de Spectrochimie des Ions
Université de Nantes, 44072 Nantes Cedex 03

G. Wlodarczak and J. Demaison
Laboratoire de Spectroscopie Hertzienne, associé au CNRS, Bât. P5,
Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France.

H. Bürger, and O. Polanz
Anorganische Chemie, FB9, Universität-Gesamthoschschule, D 42097
Wuppertal, Germany

The infrared spectra of BrCN comprising ^{79}BrCN and ^{81}BrCN have been recorded with a high resolution (0.003 cm^{-1}) FTIR spectrometer in the regions of the three bands ν_1, $2\nu_2$ and ν_3 near 2200, 700 and 575 cm^{-1}, respectively. These bands have been analyzed and more combination and overtone levels have been determined from attached hot bands. Furthermore the millimeterwave spectra of the excited vibrational states $\nu_2 = 1, 2$ and $\nu_3 = 1$ have been previously measured in the range 100-470 GHz [1].

Rotational parameters of numerous vibrational states have been determined by a combined fit of the infrared and millimeterwave data. The results will be compared with those obtained for the isoelectronic molecule OCSe.

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N15

HOW MANY ANHARMONIC RESONANCES ARE THERE IN THE WATER MOLECULE ?

V.I.Starikov, S.N.Mikhailenko

Laboratory of Theoretical Spectroscopy, Istitute of Atmospheric Optics,
1, Akademicheskii Av., 634055, Tomsk, Russia

In this work the vibrational problem for the water molecule is investigated. The large amplitude motion in the water molecule may cause new types of vibrational interactions which differ from the usual ones based on the approxime relations $\omega_1 \approx 2\omega_2$ and $2\omega_1 \approx 2\omega_3$. A large number of different types of vibrational interactions taken into account in the vibrational matrix. The influence of these interactions on the vibrational centers of the water molecule is analysed.

N16

PHOTO-ACOUSTIC MEASUREMENTS OF WATER VAPOR ABSORPTION COEFFICIENT IN UV SPECTRAL REGION

B.A. Tikhomirov, V.O. Troitskii,

V.A. Kapitanov, G.S. Evtushenko, and Yu.N. Ponomarev

Institute of Atmospheric Optics of SB RAS,

1 Akademicheskii Ave., Tomsk, 634055, Russia

The copper vapor laser with radiation frequency converter ($\lambda = 255$ nm, 271 nm, and 289 nm) is applied for ozone sounding in the atmosphere using the differential absorption technique[1]. The high precision data on absorption cross sections of O_3 and other molecules of atmospheric air, including H_2O-vapor[2], are required for correct processing of the lidar signals and obtaining of information about O_3 content in the atmosphere.

The paper presents the results of design of high-sensitive photoacoustic spectrometer of UV spectral region with copper vapor laser and radiation frequency converter. Calibration of the photo-acoustic detector was carried out using He-Ne laser ($\lambda = 3.39$ μm) and standard gas mixtures of CH_4 with N_2, H_2, and air. The measured absorption coefficient is presented as a function of the buffer gas pressure. Methodological problems of photoacoustic measurements in UV spectral region are discussed.

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N17

ROTATIONAL STATES OF MOLECULES: SPECTRA AND THE UNDERLYING CLASSICAL DYNAMICS

S.V. Petrov

Department of Chemistry, Moscow State University,
Moscow 119899, Russia

One of the possible approaches which allows to study qualitative features of the intramolecular dynamics and rovibrational spectra especially in the case when the rovibrational interaction can not be considered as a small one is presented. The proposed method is based on the construction of the classical effective rotational Hamiltonian (CERH). This construction begins with exact rovibrational classical Hamilton function: $H_{cl} = H_{cl}(q, p, J_\alpha)$, where q is a set of internal coordinates, p are corresponding momenta, and J_α are three components of total angular momentum. By definition, the CERH is determined as follows (It is the basic idea of the proposed method): $H_{cl} = H_{cl}(q_e, p_e, J_\alpha)$, where q_e and p_e are determined from the set of equations

$$\frac{dH_{cl}}{dq} = 0, \qquad \frac{dH_{cl}}{dp} = 0.$$

It is important that q_e and p_e depend on the J_α. Considering the CERH as the function of the direction of angular momentum vector (at fixed value J) I obtain immediately the so called Rotational Energy Surface (RES). It is well known that the RES is a powerful tool for qualitative analysis of a structure of molecular rotational spectra. As an example, the rotational structure of the ground vibrational state of symmetric (C_{2v}, T_d groups) tri- and tetraatomic molecules is studied. Moreover, the effective quantum rotational Hamiltonian can be found from the CERH by replacing the classical components J_α by corresponding rotational operators. This enables one to calculate rovibrational levels of energy. As an example, rovibrational spectra of some diatomics and the KCN molecule are calculated.

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Absolute Line Intensities in the ν_2 Band of $^{12}CH_3^{35}Cl$ by Diode-Laser Spectroscopy

Ghislain BLANQUET[*], Benoît LANCE[*], Jacques WALRAND[*], and Jean-Pierre BOUANICH[+].

[*] Laboratoire de Spectroscopie Moléculaire, Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles, B-5000 Namur, Belgium

[+] Laboratoire de Physique Moléculaire et Applications, CNRS, Université de Paris-Sud, Bâtiment 350, F-91405 Orsay cedex, France

With concentrations between 500 and 1000 ppt, methyl chloride (CH_3Cl) is the most abundant chlorine compound of natural origin in the earth's atmosphere. Therefore, knowlegde of accurate spectral parameters (line position, line intensity, collisional broadening) is required for investigations of atmospheric spectra. Last years, several studies have been published giving the absolute intensity of the ν_2 band of $^{12}CH_3^{35}Cl$. The values reported by different authors show large discrepancies: 29.9 ± 0.9 $cm^{-2}.atm^{-1}$ [1], 34.6 ± 2.8 [2] and 37.0 ± 1.5 [3]. The last values are deduced from low resolution measurements on natural sample of CH_3Cl. The main objective of the present investigation is to determine accurate values for the line strengths and the band strength.

Using our diode-laser spectrometer, we have measured the intensities of 100 lines in the ν_2 fundamental band in the region 1350 cm^{-1}. These lines were selected over a wide range of rotational quantum numbers ($6 \leq J \leq 42$ and $0 \leq K \leq 6$) such that they are reasonably isolated. For most of the lines, we used the equivalent width method to determine the infrared absolute intensity but for eleven lines, we have fitted the individual profile with a Voigt model by adjusting their intensity and self-broadening width. Finally, we derive a new value of the ν_2 band strength (33.46 ± 0.13 $cm^{-2}.atm^{-1}$) and the first Herman-Wallis factor $(-3.05 \pm 0.09) \times 10^{-3}$.

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Vibrational rotational relaxation of methane in a supersonic jet

D.K.Bronnikov, D.V.Kalinin, V.D.Rusanov
Russian Scientific Center: Kurchatov Institute, Moscow 123182, Russia
J.C.Hilico
Laboratoire de Physique de l'Université de Bourgogne, Dijon 21000, France
Yu.G.Selivanov
Lebedev Physical Institute, Moscow 117924, Russia

The vibrational rotational relaxation in a supersonic jet of heated methane was investigated by high-resolution diode laser spectroscopy in the 7.7 μm spectral region. Preliminary heated methane with stagnation temperature in the range 300-1000 K was expanded in a slit nozzle. The rotational distribution was measured for molecules in the ground, dyad and pentad states. Total population of each observed polyad was calculated from intensities of appropriate lines in the jet for different distances from the nozzle. The rotational relaxation of vibrationally excited and non-excited molecules was first studied with pure methane. In this case, and for different distances from the nozzle, ratio of the populations of excited and non-excited states was unchanged. To observe the energy distribution in case of vibrational relaxation, few percents of ethane (a well-known efficient catalyst for the vibrational relaxation of methane[1]) were added to methane. Under these conditions, decrease of population of vibrational excited states and increase of rotational temperature were observed. This effect of rotational heating due to the vibrational relaxation demonstrates the conversion of vibrational energy to rotational one during the process. The rates of vibrational relaxation for molecules in the dyad and pentad states were estimated from the dependance of the polyad population on distance from the nozzle.

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N20

Rotational and vibrational analysis of GeH_4, GeH_3D and $GeHD_3$ stretching overtone transitions (V=6, 7 and 8) in the visible range.

Xiao-Gang Wang[a], Dmitri Permogorov, Alain Campargue
Laboratoire de Spectrométrie Physique[c], Université Joseph Fourier/Grenoble I,
B.P.87, 38402 Saint-Martin-d'Hères, France

Hans Bürger
FB9-Anorganische Chemie, Universität-Gesamthochschule, D-42097 Wuppertal,
Germany

The high resolution spectra of the V_{Ge-H}=6, 7 and 8 stretching overtones of gaseous $^{70}GeH_3D$ and $^{70}GeHD_3$ have been recorded by intracavity laser absorption spectroscopy (ICLAS). The $^{70}GeHD_3$ spectra have been analysed as symmetric-top parallel bands. The rotational constants of $^{70}GeHD_3$ depend linearly on the stretching quantum number and from this linear relation the α_B and α_C constants have been obtained. The V=6, 7 and 8 overtone transitions of $^{70}GeH_3D$ have been rotationally analysed in the frame of the local mode model. This was known to be valid already for the V=3 overtone (H. Bürger and L.Halonen, separate poster contribution)
From the band origins of the overtone transitions of the different isotopic species of GeH_4 we have determined the three parameters of the local mode vibrational hamiltonian (a, D_e, $f_{rr'}$) and reproduced the experimental data (41 bands) within a rms deviation 0.5 cm^{-1}. These values can be used for calculating the stretching vibrational levels of $^{70}GeH_3D$ and $^{70}GeHD_3$. the comparison between the calculated and observed values will be discussed. This work is supported by the European Community (Contract CHRX-CT94-0665).

N21

The octad of methane (and associated hot bands)

J.C. Hilico *and* S.Toumi
Laboratoire de Physique de l'Université de Bourgogne, Dijon 21000, France
L.R.Brown
Jet Propulsion Laboratory, Pasadena, California 91109, USA
A.S.Pine
Molecular Physics Division, NIST, Gaithersburg, Maryland 20899, USA

The eight bands ($3\nu_4$, $\nu_2+2\nu_4$, $\nu_1+\nu_4$, $\nu_3+\nu_4$, $2\nu_2+\nu_4$, $\nu_1+\nu_2$, $\nu_2+\nu_3$, $3\nu_2$) appearing in the (2.2 - 2.8 μm) spectral region are analyzed simultaneously in polyad scheme. Experimentally, several Fourier transform spectra were recorded at the K.P.N.O., one of which at 193 K. Five windows covering the Q-branches of $3\nu_4$ (two), $\nu_2+2\nu_4$, $\nu_1+\nu_4$ and $\nu_3+\nu_4$ were also recorded with a difference-frequency laser spectrometer. Relative absorbance measurements of the latter spectra at T=296 and 80 K provided a direct determination of J. Theoretically, the extrapolation method is applied for energy levels with a partial fourth order Hamiltonian containing 323, but only 117 NEW parameters in order to reproduce more than 5000 transitions (up to J=16) and 1200 lines of the (octad-dyad) hot band system . The strong encountered interactions lead to considerable intensity perturbations needing 15 dipole parameters to explain the octad intensities. On the other hand, the 4 first order pentad dipole parameters[1] are already sufficient to reproduce all the hot band intensities. The preliminary results of this work have been used to analyze the spectra obtained during the collision of comet SL-9 with Jupiter[2]. Part of the research reported in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

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N22

High resolution spectroscopy of small aromatic molecules in supersonic molecular beam

Maurizio Becucci*, Gianni Pietraperzia°, Erik R. Kerstel[•] and Emilio Castellucci*°

* LENS, Università di Firenze, Largo E. Fermi 2, 50127 Firenze, Italy

° Dip. Chimica, Università Firenze, via G. Capponi 9, 50121 Firenze, Italy

[•] CIO, University of Groningen, 9747 AG Groningen, The Netherlands

We are reporting some results obtained with the new high resolution molecular beam spectrometer built at the LENS laboratory. The apparatus is currently used for the study of spectroscopy and dynamics of electronic excited states of small-medium size molecules and their Van der Waals complexes. The experimental setup includes a LIF detector (photomultiplier) and a optothermal detector (bolometer) for the energy content of the molecular beam. This allows us to monitor the radiative (fluorescence) and non-radiative relaxation processes (i.e., IVR, photodissociation)[1]. The optothermal detector gives a large flexibility at this apparatus because it can be successfully used in a broad spectral region (IR to UV)[2].

We will show the high resolution spectra of aniline (single molecule and VdW complexes with rare gas) and s-tetrazine in the $S_1 \leftarrow S_0$ electronic transition. The spectrum of s-tetrazine is particulary interesting because we are demonstrating that even for molecules with an extremely low quantum yeld of fluorescence, using the optothermal detector, we are able to obtain high quality data.

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N23

Laboratory and Atmospheric Spectra of the ClONO$_2$ ν_5
Band Around 563 cm^{-1}: New Quantitative Spectroscopic
Measurements of Stratospheric Chlorine Nitrate

J. ORPHAL[§], D. G. JOHNSON[†], K. CHANCE[†], G. GUELACHVILI[‡],
K. W. JUCKS[†], M. MORILLON-CHAPEY[‡], AND W. A. TRAUB[†]

[§] *Institute of Environmental Physics, University of Bremen, P.O. Box 330440,
28334 Bremen, Germany, e-mail: orphal@gome1.physik.uni-bremen.de*
[†] *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cam-
bridge, MA 02138, USA, e-mail: dgj@cfa.harvard.edu*
[‡] *Laboratoire de Physique Moléculaire et Applications, CNRS, Bât. 350,
91405 Orsay Cedex, France, e-mail: guelac@lpma.u-psud.fr*

Abstract

Accurate laboratory measurements of ClONO$_2$ infrared absorption cross
sections at atmospheric temperatures and pressures have been carried out
using the step-scan Fourier-Transform Spectrometer at LPMA in Orsay. The
ClONO$_2$ sample was synthesized using the low-temperature reaction of Cl$_2$O
and N$_2$O$_5$, followed by distillations. Absorption spectra were recorded at 223
K and 231 K, with 0.02 cm^{-1} unapodized resolution, using mixtures of
ClONO$_2$ with N$_2$ (total pressures 2.3 hPa, 45.3 hPa, 85.2 hPa, and 137.4 hPa,
corresponding to stratospheric pressures between 15 km and 40 km of alti-
tude). These spectra were used to determine pressure-dependent ClONO$_2$
absorption cross sections in the ν_5 band between 540 cm^{-1} and 580 cm^{-1}.
Measurements of stratospheric ClONO$_2$ emission were made with the SAO
Far Infrared Spectrometer (FIRS-2), a rapid-scan Fourier-Transform Spec-
trometer with 0.004 cm^{-1} unapodized resolution, operating between 350 cm^{-1}
and 700 cm^{-1}. The instrument was launched on a balloon in Fort Sumner
(Maryland, USA, 34.5°N and 104.2°W) on May 22, 1994, and recorded
stratospheric emission spectra for tangent heights between 17 km and 38 km.
In these spectra, the ν_5 band could clearly be identified for the first time and
was used to determine stratospheric ClONO$_2$ mixing ratios.
The preliminary results are compared to simultaneous ClONO$_2$ quantitative
measurements during this balloon flight, using the ClONO$_2$ ν_4 Q-branch
absorption around 780 cm^{-1}.

THE ROTATION SPECTRUM OF THE EXCITED VIBRATIONAL STATES OF DCOOH AND ASSIGNMENT OF OPTICALLY PUMPED LASER TRANSITIONS

O.I.Baskakov

Faculty of Quantum Radio Physics, Kharkov State University, Svobody Sq. 4, 310077 Kharkov, Ukraine

The spectrum of DCOOH which is a slightly asymmetric top plane molecule has been measured in separate parts of the frequency region between 175 and 330 GHz. From the measurements it was possible to assign 63 ^{a}R-type transitions in ν_8 (874.8 cm^{-1}) state, 47 transitions in ν_6 (970.9 cm^{-1}) and 48 in ν_5 (1140.8 cm^{-1}). Any appreciable interactions of these states with other excited states have not been found. Therefore rotational and centrifugal distortion constants have been obtained using Watson's theory for asymmetric rotors.

The derived molecular constants in the ν_6 state enabled some optically pumped laser transitions from Ref. (1) to be assigned

398 263. 8 MHz	$17_{14,4} \rightarrow 18_{14,5}$
420 404. 0 MHz	$18_{14,4} \rightarrow 19_{14,5}$
469 064. 7 MHz	$20_{5,15} \rightarrow 21_{5,16}$
691 985. 3 MHz	$30_{7,23} \rightarrow 31_{7,24}$

In addition, improved ground state parameters and ν_6 band center

$$\nu_6 = 29\ 106\ 543 \pm 70\ \text{MHz}$$

have been obtained.

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Diode Laser Spectrum of Cis-1,2 Difluoroethylene at 1131 cm^{-1}; Determination of Ground and v_{10} = 1 State Parameters

P. Stoppa, S. Giorgianni and S. Ghersetti

Dipartimento di Chimica Fisica, Università di Venezia, D.D. 2137, I-30123
Venezia, Italy

Cis-1,2 Difluoroethylene has been prepared, and gas-phase infrared spectrum has been recorded in the v_{10} band region between 1110 and 1152 cm^{-1}, at a resolution of about 0.002 cm^{-1}, using a tunable diode laser spectrometer. This compound is a planar molecule belonging to the C_{2v} point group and the v_{10} vibration of simmetry species B_1 yields an **a**-type band.

Since the asymmetry parameter κ is -0.841, this molecule approaches to a prolate symmetric top and the spectrum of the **a**-type absorption would correspond to that of a parallel band. The Q branch is characterized by a series of J-resolved $^Q Q_K$ manifolds whose interpretation represented the starting point of the analysis. The resolved structure in the P, Q, and R branches led to the identification of more than 2000 lines with $J \leq 67$ and $K_a \leq 26$.

From a simultaneous fit of the present GSCD, together with a few literature microwave data, a set of ground state constants up to the fourth order has been obtained using Watson's A-reduction Hamiltonian in the I^r representation. A least-squares fit of the assigned transitions provided a set of upper state constants for the v_{10} band.

Experimental and simulated spectra, details of the interpretation, and results obtained from the analysis will be presented.

STRUCTURAL DETERMINATION OF H_2SiO USING SUBMILLIMETRE-WAVE SPECTROSCOPY

S. Bailleux, M. Bogey, C. Demuynck, J.L. Destombes, B. Delcroix

and A. Walters

Laboratoire de Spectroscopie Hertzienne, Université de Lille I, Bât. P5,

59655 Villeneuve d'Ascq, France

Although the theoretical structure of silanone has been calculated at various ab initio theory levels, there has been no comparative experimental determination due to the difficulty of observing this reactive species in the gas phase. We produced silanone by means of an "abnormal-glow" electric discharge in a mixture of silane and oxygen and subsequently measured the rotational submillimetre-wave spectrum of the parent species and of four other isotopomers ($H_2{}^{29}Si{}^{16}O$, $H_2{}^{30}Si{}^{16}O$, $H_2{}^{28}Si{}^{18}O$ and $D_2{}^{28}Si{}^{16}O$) The spectra were fitted to Watson's A-reduced Hamiltonian in order to determine rotational and centrifugal distortion constants. Difficulties in fitting the components of certain close-lying K_a doublets were shown to be due to a Stark interaction with the electric field created by the discharge. The fitted rotational constants were used to calculate an r_m^{ρ} structure of this elusive molecule. The bond lengths and angles have been determined as : Si=O 1.516 Å, Si-H 1.472 Å, < HSiH 112.0°.

Microwave Spectra of Methylpyrrole Complexes
with One and Two Argon Atoms

S. R. HUBER AND A. BAUDER

Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland

The microwave spectra of the 1-methylpyrrole–argon and the 1-methylpyrrole–(argon)$_2$ complexes have been measured and analysed in a pulsed molecular beam Fourier transform spectrometer in the frequency range of 8–18 GHz. For the complex with one argon atom, the rare gas is located above the aromatic ring plane similar to the pyrrole–argon complex. For the 1-methylpyrrole–(argon)$_2$ complex, the argon atoms are located symmetrically on each side of the ring plane.

The internal rotation of the methyl group in the 1-methylpyrrole monomer is hindered by a small sixfold barrier. On complexation with two argon atoms, the symmetry is not changed and the potential is similar to that of the monomer. For the complex with one argon atom, the symmetry is reduced and a threefold contribution has to be included in the potential function. The internal rotation splittings of the complexes with argon in the torsional ground state have been analysed and the potential function has been fitted.

In addition, the spectra of the isotopomer with a partially deuterated methyl group and its complexes with one or two argon atoms have been measured. The observed transition frequencies will be used to determine the equilibrium position of the methyl group with respect to the ring plane.

THE MICROWAVE SPECTRUM
OF 1-CHLORO-1,2,2,2-TETRAFLUOROETHANE

A. Aguado, S. Blanco, J. C. López and J. L. Alonso

Departamento de Química Física, Facultad de Ciencias, Universidad
de Valladolid, 47005 Valladolid, Spain

The microwave spectrum of 1-chloro-1,2,2,2-tetrafluoroethane has been analyzed in the frequency region 12-52 GHz using FT-MW and Stark modulation spectrometers. The spectra for the ground state of ^{35}Cl and ^{37}Cl isotopomer and for the two lowest excited states of the CF_3 torsional vibration of ^{35}Cl have been measured up to $J=60$. Chlorine nuclear quadrupole coupling constants have been determined from a first order analysis to be $\chi_{aa}=-34.25(5)$ MHz, $\chi_{bb}=4.51(5)$ MHz, and $\chi_{cc}=29.74(5)$ MHz for ^{35}Cl. Rotational constants and quartic centrifugal distortion constants have been determined from central frequencies. No CF_3 group internal rotation splitting has been observed and relative intensity measurements give a rough estimate of the barrier to internal rotation of 4.0 ± 1.5 kcal mol^{-1}.

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SIDEBAND SPECTROSCOPY IN THE VISIBLE
WITH A TUNABLE MODULATOR

U. Häring, W.A. Kreiner,
Universität Ulm, Abteilung Chemische Physik,
D-89069 ULM, Germany
G. Magerl, and W. Schupita
Technische Universität Wien, Institut für Nachrichtentechnik,
A-1014 WIEN, Austria

Phase modulation at microwave frequencies has been applied to the radiation of a cw ring dye laser in order to observe sideband spectra. In order to do this use was made of the electrooptic effect in a lithium tantalate bulk crystal.

This spectroscopic technique allows relative frequencies to be determined instead of the more usual wavelengths.

The design of the modulator allowed conservation of the phase matching condition (equality between light velocity and phase velocity of the microwave in the crystal) at microwave frequencies between 11 and 17 GHz. Sideband power of the order of 1 mW was produced.

By scanning spectra simultaneously with two different sidebands and superimposing them on the same recording we were able to determine the frequency separation of hyperfine components of several iodine transitions.

The distance between the a_1 component of the transition P62 (17-1) of $^{127}I_2$ and the b_{15} component of R66 (17- 1) [tentative assignment] was found to be

$$R66(17-1)b_{15} - P62(17-1)a_1 = 26164.6(43) MHz.$$

N30

THE NO DIMER. I - ANALYSIS OF THE ν_5 BAND.

A. Dkhissi[*], A. Perrin[**], P. Soulard[*] and N. Lacome[*]

[*]Laboratoire de Spectrochimie Moléculaire, URA CNRS 508, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris cedex 05, France

[**]Laboratoire de Physique Moléculaire et Applications, UPR CNRS 136, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris cedex 05, France

The ν_5 band of $(NO)_2$ centered at 1789 cm^{-1} has been recorded with a Fourier transform spectrometer (Bruker IFS 120 HR) at a resolution of 0.008 cm^{-1}. For this purpose a multipass White-type cell cooled down to 130 K, was used and the optical path length was 16 meters.

Several spectra were recorded for total pressures ranging from 30 to 90 mbar and temperatures varying from 130 to 150 K.

In the case of the ν_5 transition, a predissociation phenomenon makes the rotational structure unresolved. Therefore, the values of the rotational constants of the upper state were adjusted in order to achieve the best fit of the synthetic band profile so-obtained, to the observed spectrum.

The dissociation energy of the dimer was determined by analyzing the variation, at constant density, of the band intensity. A value of 764 cm^{-1} was obtained, in good agreement with previous determinations.

The equilibrium constant of the reaction $2NO \rightleftharpoons (NO)_2$ was calculated, making it possible to derive the value of the transition dipole moment. Finally, from the fit of the band profile an estimate of the predissociation time could be obtained and was found to be $\tau = (59 \pm 13)$ ps.

N31

INVESTIGATION OF RAMAN Q BRANCH PROFILES OF H_2 PERTURBED BY N_2. INTERPRETATION IN TERMS OF SPEED DEPENDENT BROADENING AND SHIFTING.

P. SINCLAIR, J.P. BERGER, X. MICHAUT,
R. SAINT-LOUP and H. BERGER
Université de BOURGOGNE - 21000 DIJON FRANCE

P. JOUBERT, J. BONAMY and D. ROBERT
Université de FRANCHE-COMTE - 25030 BESANCON FRANCE

H_2 is of particular interest in aerospace research with regard to cryogenic combustion. Since N_2 is the predominant perturber in the exhaust of CH_4/air flames we have investigated the line broadening and shifting of H_2 perturbed by N_2.

The experiments were performed at temperatures of 300, 800 and 1200K with the aim of extrapolating the broadening coefficients to flame temperatures of the order of 2000 K.

Previous studies of H_2 perturbed by rare gases have shown two unusual features.[1,2] The line profiles were asymmetric and the broadening increased non-linearly with the perturber concentration. The data were explained using a lineshape model which predicts inhomogeneous broadening due to the speed dependence of the shift coefficient.[3]

Since the rare gas studies were performed the maximum sample temperature has been raised from 800 to 1200 K. At 1200 K the spectra of H_2 highly diluted in N_2 are very asymmetric. These asymmetries have been explained by including speed dependent broadening, as well as speed dependent shifting, in the lineshape model.

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[2] J. Ph. Berger, R. Saint-Loup, H. Berger, J. Bonamy, and D. Robert, Phys. Rev. A **49**, 3396 (1994).

[3] D. Robert, J.M. Thuet, J. Bonamy and S. Temkin, Phys. Rev. A, **47**, 771 (1993).

N32

PRESSURE BROADENING AND LINE COUPLING FOR VARIOUS Q BRANCHES OF CO_2 IN HELIUM

J. Boissoles and F. Thibault

Département de Physique Atomique et Moléculaire, URA 1203 du CNRS, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France.

C. Boulet

Laboratoire de Physique Moléculaire et Applications (Laboratoire associé aux Universités Paris-Sud et P. et M. Curie), UPR 136 du CNRS, Université de Paris-Sud, Centre d'Orsay, Bât. 350, 91405 Orsay Cedex, France.

We present experimental and theoretical results for CO_2-He absorption near 15 μm for various infrared bands of different symmetry species. Measurements were carried out with a Fourier tranform interferometer at room temperature for pressures up to 50 atm. Computations, within the framework of the impact approximation, take into account line mixing effects. The relaxation matrix is modelled with the Energy Corrected Sudden (ECS) approximation derived from the Infinite Order Sudden (IOS) formalism proposed by Green[1] which is valid for all type of vibrational band. The basic fundamental rates used were deduced from a fitting procedure[2], and the diagonal relaxation matrix elements (the linewidths) are given by the sum rule (which is expected to be fairly accurate for the CO_2-He system). The computed absorption coefficient is expressed as a summation of equivalent lines[3] for which each profile has the Rosenkranz form (but not the same meaning).

Strong deviations from the sum of the Lorentz contours are observed in the experimental spectra, and the ECS calculations account for these experiments quite satisfactorily.

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[2] - J. Boissoles, F. Thibault, R. Le Doucen, V. Menoux, C. Boulet, J. Chem. Phys. **101**, 6552 (1994).

[3] - J. Boissoles, F. Thibault, R. Le Doucen, V. Menoux, C. Boulet, J. Chem. Phys. **100**, 215 (1994).

Experimental and theoretical investigation of the broadening and shifts of spectral lines of SO_2, NO_2, and H_2O

B. Sumpf [*#], O. Fleischmann [*], V.V. Pustogov [*], H.-D. Kronfeldt [*],
V.V. Lazarev [**], Yu.N. Ponomarev [**], V.N. Stroinova [***]

[*] Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1
Straße des 17. Juni 135, D-10623 Berlin, Germany
e-mail: tdlas@marie.physik.tu-berlin.de
[**] Institute of Atmospheric Optics,
Siberian Branch, Russian Academy of Sciences,
1, Akademicheskii Ave., 634055 Tomsk, Russia
[***] Polytechnical University,
30 Lenin Ave., 634004 Tomsk, Russia

In this paper we present experimental and theoretical investigations concerning line broadening of spectral lines in the v_1 and v_3 bands of SO_2 and the v_3 band of NO_2 measured with a tunable diode laser spectrometer (Berlin group) and values for the line broadening and shift from the v_1+3v_3 band of H_2O obtained with a photo-acoustic spectrometer (Tomsk groups). The experimental values include collisions with nitrogen and air. In the case of water vapour we investigated the temperature dependence of the broadening and shifts in the range from 270 up to 370K. Experiments on the temperature dependence of the broadening coefficients in the v_3 band of SO_2 between 240 and 350K were carried out, currently.

The experimental results are compared with data obtained from a modified version of the Anderson-Tsao-Curnutte theory neglecting Anderson's interruption procedure and taking into account the trajectory curvature of colliding particles.

Additionally, we will present experimental and theoretical broadening and shift coefficients for collisions with noble gas perturbers, i.e. helium, neon, argon, krypton, and xenon.

Temperature dependence of line shift and line broadening parameters measured with a tunable diode laser (TDL) spectrometer

T.Y. Wang, Th. Giesen, R. Schieder and G. Winnewisser

I. Physikalisches Institut der Universität zu Köln,
Zülpicher Str. 77
50937 Köln, Germany.

A newly constructed multiple traversal absorption cell (134 m optical length) has been combined with the high resolution frequency stabilized TDL spectrometer in order to study pressure effects in the temperature range between 150 K and 300 K. Line shifts and line widthes have been obtained with a 1 MHz accuracy. The temperature can be stabilized within ± 0.5 K over the whole length of the cell. The construction of the cell, including cooling, heating, and control system will be reported in detail.

First measurements of some weakly bound molecular complexes at low temperature will be presented. Line broadening and shifting as a function of buffer gas pressure and temperature have been derived from these spectra.

N35

LINE-MIXING AND NON LINEAR DENSITY EFFECTS IN CO_2-He v_3 AND $3v_3$ INFRARED BANDS UP TO 1000 BARS

L. Ozanne, C. Brodbeck, Nguyen-Van-Thanh, J.P. Bouanich,
J.M. Hartmann, and C. Boulet

Laboratoire de Physique Moléculaire et Applications (CNRS UPR 136)
Université Paris-Sud (bât 350)
Campus d'Orsay
91405 Orsay Cedex, France.

We present high density experimental and theoretical results on CO_2-He absorption in the n_3 and $3n_3$ infrared bands. Measurements have been made at room temperature for pressures up to 1000 bars in both the central and wing regions of the bands. Computations are based on an impact line-mixing approach in which the relaxation operator is modelled with the Energy Corrected Sudden (ECS) approximation. Comparisons between experimental and calculated results demonstrate the accuracy of the ECS approach when applied to band wings and band centers at moderate densities. On the other hand, significant discrepancies appear at very high pressures. They are attributed to a number of reasons which include non linear density dependence due to excluded volume effects, contribution of vibration to the relaxation matrix, and incorrect modelling of interbranch mixing. We also tested asymptotic expansions in the wing, which point out the influence of interbranch couplings.

TUNABLE DIODE LASER BASED SYSTEMS FOR ANALYTICAL APPLICATIONS

A.I.Nadezhdinskii

General Physics Institute, Russian Academy of Sciences,
Moscow

Family of Tunable Diode Laser based systems was developed for different Applications. The system are operating under full computer control. Due to the model proposed, Diode Laser frequency tuning can be predicted with high precision. Computer determines laser operation mode, identifies observed spectral line,
and using spectral data base information, calculate concentration of molecules to be measured. New generation of "Chernin" multipass optical cells (aberration "free", insensitive to vibration, up to 1000 passes) was developed and incorporated in the TDL based systems. The instruments developed were used in atmosphere monitoring, medicine, high technology, ets.

N37

The CN mode of HCN: A comparative study of the variation of the transition dipole and the Herman-Wallis constants for seven isotopomers and the influence of vibration-rotation interaction

A.Maki,[w] W. Quapp,[l] S.Klee,[g] G.Mellau,[g] S.Albert[g]

[w]15012 24 Ave. S. E., Mill Creek, Washington 98012, U.S.A.

[l]Mathematisches Institut, Universität Leipzig,
Augustus-Platz, D-04109 Leipzig, Germany

[g]Physikalisch-Chemisches Institut, Justus-Liebig-Universität
Heinrich-Buff-Ring 58
D-35392 Gießen, Germany

The electric dipole transition moment and vibration-rotational constants of the CN stretching bands of HCN and six other isotopomers are reported. This CN mode of HCN at $2\,097\,\text{cm}^{-1}$ is a notoriously weak mode with a curious behaviour of the infrared intensity of some rotational lines. There is a gap of the intensity of some lines near J=7 in the R branch. The gap goes to R(4) in $HC^{15}N$, R(1) in $H^{13}CN$, and it jumps to P(1) in $H^{13}C^{15}N$. A similar behaviour is shown by the hot band transitions 01^11-01^10.

We give an explanation using the theory of line intensities with the inclusion of vibration-rotation interaction[1] for triatomic molecules. The unusually small transition moment coupled with the large dipole moment of HCN (2.98 debye) results in a very large value for the first Herman-Wallis factor A_1 and distorts the shape of the intensity envelope of the band. There is also a contribution from the Coriolis interaction with the strong ν_2 transition through the ζ_{23} interaction constant.

A formula for the first Herman-Wallis coefficient[2] was tested, within the accuracy of our measurements, for the correct relationship between the Herman-Wallis constant and the transition dipole.

[1]N. Jacobi and J. H. Jaffe, *J. Mol. Spect.*, **10** 1-11 (1963)
[2]J. K. G. Watson *J. Mol. Spect.*, **125** 428-441 (1987)

N38

VISIBLE ABSORPTION SPECTROSCOPY USING FTS AND A MULTIPASS OPTICS GAS CELL

D. Newnham, M. Page, and J. Ballard

Rutherford Appleton Laboratory

Chilton, Didcot, Oxon, OX11 0QX, U.K.

The performance of a long optical pathlength (up to 1 km) coolable gas cell[1] in the near-infrared, visible, and near-UV has been assessed. The White cell is optically interfaced to the Bruker IFS 120 HR Fourier transform spectrometer at RAL for high resolution broadband studies of weakly absorbing molecular species at pressures of up to 5 bar. The potential of this experimental facility for quantitative spectroscopy in the 300 to 1200 nm spectral region is discussed in terms of the achievable pathlength, spectral resolution, signal-to-noise ratio, and baseline stability. Preliminary measurements are reported for the band strengths and line parameters of the highly forbidden A and B 'atmospheric band' transitions of O_2, and vibrational overtone spectra of CH_4.

[1] - J. Ballard, K. Strong, J. J. Remedios, M. Page, and W. B. Johnston, JQSRT, 52, 677 (1994).

OPTIMISATION OF AN ACOUSTOOPTICAL DEVICE FOR HETERODYNE ANALYSIS

M.E. Faye, S. Kalite, A. Delahaigue

Groupe de Spectrométrie Moléculaire et Atmosphérique

URA CNRS D1434

Faculté des sciences, B.P. 347, 51062 Reims cedex, France.

Heterodyne detection at 10 μm and its sequential spectral analysis have shown the feasibility of laboratory and atmospheric spectroscopy.

To improve the spectrum acquisition time, we developed an acousto-optical analysis with an acousto-optic spectrometer (AOS). The AOS with a bandwidth of 900 MHz and a 1 MHz resolution has been lent by the Meudon observatory.

This AOS has to be adapted to the heterodyne set-up (mechanical modulation, spectra acquisition speed, and number of bits of the digital converter) so as not to degrade the heterodyne signal to noise ratio.

We have studied the main noise factors in the acousto-optic device to determine the optimal experimental configuration. We choose a 16 bits converter and record at a rate of 22 ms. The recorded elementary spectra are summed during a total acquisition time ranging from a few seconds to a few minutes.

The obtained results show the multiplex advantage and the improvement brought by this technique. This is particularly important for the case of atmospheric measurements.

INFRARED STIMULATED EMISSION OF O_3 IN INERT MATRICES

D. Jasmin, V. Raducu, P. Brosset, R. Dahoo, B. Gauthier-Roy

and L. Abouaf-Marguin

L. P. M. A. 4, place Jussieu 75252 Paris cédex 05

Vibrational relaxation study of ozone in rare gaz matrices through pump-probe technique led to observation of a strong chaotic fluorescent emission. The latter corresponds to the $2\nu_3 \rightarrow \nu_3$ (1003 cm^{-1}) transition which follows pumping of the $\nu_1 + \nu_3$ vibrational mode (2100 cm^{-1}) at 5 K by a pulsed (5 ns) tunable laser (Quantel) and presents all the characteristics of a stimulated emission.

Fluorescence is observed above a threshold pump energy and its intensity is proportional to that of the pump. It is delayed with respect to the pump, the delay time as well as its yield decreasing from xenon to neon and its time duration is less or equal to that of the pump pulse.

Coupled differential equations modeling the time dependence of the level populations are numerically solved to explain experimental results such as the correlations between the delay time, threshold pump energy and the matrix.

ν_1, ν_2, ν_3 (cm-1)

1, 0, 1 (2091.4, 2090.3)
0, 3, 0 (~ 2067)
0, 0, 2 (2032.1, 2030.6)

1, 1, 0 (1788.4)
0, 1, 1 (1711.4)

0, 2, 0 (~ 1381)

1, 0, 0 (1097.3, 1096.6)
0, 0, 1 (1028.8, 1027.9)

0, 1, 0 (699.1)

0, 0, 0

993.8

STIMULATED EMISSION

~ 686

691.1
690.4

682.6
681.5

EXCITATION

1003.3
1002.7

~ 690

1020.3

PROBE

1028.8
1027.9

699.1
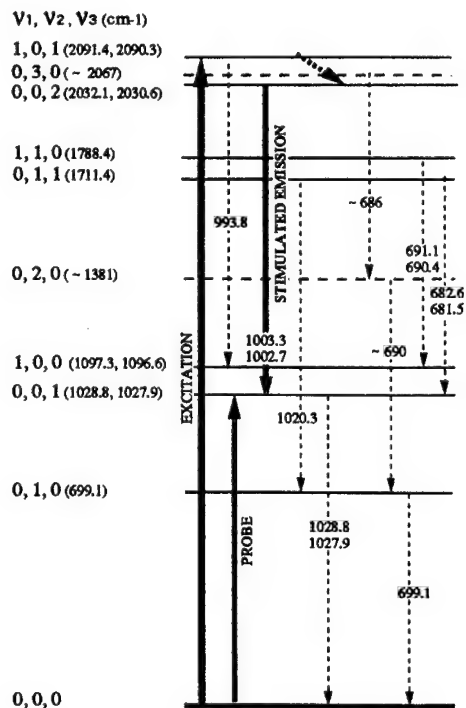
Energy levels of O3 in xenon matrix

LONG-PATH FTIR SPECTROSCOPY AT VERY LOW TEMPERATURES

A.R.W. McKellar

Steacie Institute for Molecular Sciences

National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

High resolution spectroscopy of complexes is now *the* most direct and precise means to determine intermolecular potential energy surfaces for small to medium systems. Most IR spectroscopy of complexes exploits the advantages of supersonic jets, namely increased concentration of complexes and low internal temperatures. But there are advantages to the alternate technique of a static cell containing equilibrium gas at low temperature. These include achievement of long absorption paths and easy interfacing with a wide-range FTIR spectrometer. For many complexes, it is practical and desirable to study *all* of the spectrum -- even high rotational and vibrational levels not accessible in a jet -- because the aim is to determine the entire attractive portion of the potential surface. The higher temperatures available in a static cell are then an advantage, particularly if basic structural data are known from jet spectra and good theoretical tools are available.

A new absorption cell interfaced with a Bomem DA3.002 Fourier transform spectrometer has recently been put into operation. It is 5 m long and is capable of paths of up to 200 m at temperatures as low as 20 K. Compared to its 3.5m long predecessor, it gives longer paths, and, more importantly, has a larger optical aperture (f/25 vs. f/55). The result is improved sensitivity and the capability of higher spectral resolution. The enhanced throughput enables much better performance in the difficult "far" infrared region below the cutoff (≈ 1800 cm^{-1}) of the InSb detector. New results described here concern CO-H_2 (the two most abundant interstellar molecules), CH_4-Ar, CH_4-H_2, and $(NO)_2$.

High resolution IR study of the Coriolis coupling between ν_3 and ν_9 in methylene chloride.

Marcel Snels

Istituto per Materiali Speciali, CNR

Area Industriale di Tito Scalo

I-85050 Potenza, Italy

The infrared spectra of the ν_3 and ν_9 bands of isotopically pure $CH_2^{35}Cl_2$ have been recorded at a resolution of 0.0025 cm^{-1} in the range 600-800 cm^{-1} with the Bruker IFS 120 HR Fourier Transform interferometer in Wuppertal. The Coriolis coupling between the two CCl_2 stretching fundamentals ν_3 and ν_9 has been investigated. An effective coupling constant $\xi_{3,9}^c = 0.20101(3)$ cm^{-1} ($\zeta_{3,9}^c = 0.98$) was obtained from a rotational analysis of spectra recorde at room temperature. From relative intensities the ratio of the vibrational transition moments of the fundamentals ν_3 and ν_9 could be estimated as

$$\left| \frac{\mu_3}{\mu_9} \right| \cong 0.3 \pm 0.05$$

and the sign of

$$\xi_{3,9}^c \left(\frac{\mu_3}{\mu_9} \right)$$

was found to be negative. Excited state constants up to quartic terms have been obtained for both fundamental bands, using Watson's A-reduction Hamiltonian in the I^r representation. The standard deviation of the fit was $0.44 \cdot 10^{-3}$ cm^{-1}.

P1

INVITED LECTURE

P. Thaddeus
Smithsonian Astrophysical Observatory
Center for Astrophysics
60 Garden Street, 02138 Cambridge
Massachussetts, USA

P2

Interferometry and Optics with Laser prepared Atoms

W. ERTMER
Institut für Quantenoptik,
Universität Hannover,
Welfengarten 1, 30167 Hannover, Germany

Recent advances in laser cooling and manipulation of neutral atoms allow the preparation of very cold atomic ensemble at very high density. On the other hand several new schemes have been developed for coherent atom optical elements. This allows the generation of novel cavities for atomic de Broglie waves. In addition it became possible to trap and to image single neutral atoms in magnetooptical traps. This offers totally new regimes in atom optics and atom interferometry.

Q1

MICROWAVE SPECTRUM, CONFORMATION, INTRAMOLECULAR
HYDROGEN BONDING AND *AB INITIO* CALCULATIONS FOR
ETHYLENE GLYCOL VINYL ETHER[1]

K.-M. Marstokk and Harald Møllendal

Department of Chemistry, University of Oslo, P. O. Box 1033 Blindern

N-0135 Oslo, Norway

The microwave spectra of ethylene glycol vinyl ether and one deuterated species (hydroxyl group) have been investigated in the 26.0 - 39.0 GHz spectral region at −15 °C. One rotamer was assigned. This rotamer is stabilized by an intramolecular O–H ⋯ O hydrogen bond formed between the hydrogen atom of the hydroxyl group and the oxygen atom of the ether group. The C–C–O–C=C chain of atoms is practically planar with the double bond and the O–CH$_2$ bonds in a *syn* conformation. The O–CH$_2$–CH$_2$–O link is in a *gauche* conformation allowing the hydrogen bond to be formed. Absolute intensity measurements indicate that this rotamer is at least 3 kJ mol^{-1} more stable than any other rotameric form of the molecule. The microwave work has been assisted by infrared spectra of the gas as well as *ab initio* computations made at the MP2/6-31G** level of theory.

[1]K.-M. Marstokk and H. Møllendal, In press, Acta Chem. Scand.

Q2

THE INFRARED SPECTRUM OF THE AsH RADICAL IN ITS
$X^3\Sigma^-$ STATE,
RECORDED BY LASER MAGNETIC RESONANCE

Kristine D. Hensel, Rebecca A. Hughes, and John M. Brown
Physical and Theoretical Chemistry Laboratory
South Parks Road
Oxford, UK OX1 3QZ

The infrared spectrum of AsH in its ground $^3\Sigma^-$ state has been recorded using CO laser magnetic resonance (LMR), and the data have been fit in conjunction with data from previous far-infrared LMR [1] and infrared diode laser studies[2]. Several molecular parameters of AsH have been determined for the first time. In particular, arsenic nuclear hyperfine structure has been resolved, and the observation of the v=2-1 and 3-2 hot bands of AsH has allowed an accurate determination of the vibrational anharmonicity, $\omega_e x_e$. Since Lamb-dip spectra have been recorded, other molecular parameters have been determined more accurately, and $\Delta\Omega = \pm 1$ transitions of AsH in its $X^3\Sigma^-$ state have been measured. Attempts to assign additional signals to rotational-vibrational transitions in AsH_2 are in progress.

[1] K. Kawaguchi and E. Hirota, *J. Molec. Spectrosc.* **106**, 423 (1984).
[2] J.R. Anacona, P.B. Davies, and S.A. Johnson, *Mol. Phys.* **56**, 989 (1985).

Q3

THE B²Σ INTERACTION POTENTIAL OF LiAr
DEDUCED FROM LASERSPECTROSCOPIC DATA

R. Brühl and D. Zimmermann
Institut für Strahlungs- und Kernpyhsik
Technische Universität Berlin
Hardenbergstr. 36, D-10623 Berlin

Our previous measurements of the absorption spectrum of LiAr due to the transition $A^2\Pi \leftarrow X^2\Sigma$ /1/ have been extended to the region of the transition $B^2\Sigma \leftarrow X^2\Sigma$. The rotational structure of several vibrational bands leading to the levels v' = 1, 2 and 3 of $B^2\Sigma$ could be analyzed for both isotopomers ^{7}LiAr and ^{6}LiAr, thus allowing a determination of the vibrational numbering. For the $B^2\Sigma$ interaction potential we use a Lennard-Jones (8, 6) potential as a rough first approximation with $C_6 = 6.51 \cdot 10^6$ cm^{-1} Å^6 and $C_8 = 1.71 \cdot 10^8$ cm^{-1} Å^8 as our preliminary results, leading to a well-depth of (38 ± 3) cm^{-1} and an equilibrium distance of 5.92(10) Å. In addition, further vibrational levels of $A^2\Pi$ with v' = 9...11 have been observed, but have not been analyzed completely due to local perturbations. Up to now, our experimental data don't show any indication of an avoided crossing between $B^2\Sigma$ and $A^2\Pi_{1/2}$, being predicted by theoretical calculations.

/1/ R. Brühl and D. Zimmermann, Chem. Phys. Lett. 233 (1995) 455

Q4

THE LONG-RANGE POTENTIAL OF THE
K_2 $X^1\Sigma^+_g$ ELECTRONIC STATE UP TO 15 Å

C.Amiot[1], C.E.Fellows[2] and J.Vergès[1]

[1] Laboratoire Aimé Cotton, Bâtiment 505, Campus d'Orsay
91405 Orsay Cedex, France
[2] Laboratorio de Espectroscopia e Laser, Universidade Federal
Fluminense, 24000 Niteroi, RJ, Brasil

K_2 molecules, produced in a heat pipe oven, are excited by the radiations emitted by a Ti:Sa laser (Coherent Radiation model 899-21) between 731 nm and 755 nm. The laser, delivering 2.3 W, operates in monomode and frequency stabilized conditions. The fluorescence light, due to the $A\ ^1\Sigma^+_u \rightarrow X^1\Sigma^+_g$ system, is recorded by high resolution Fourier transform spectroscopy. Ground state vibrational levels are observed up to v=81, corresponding to an internuclear distance of 15.4 Å and to 99.96 % of the potential energy well depth.

A long-range study of the potential energy V, using the formalism of Le Roy [1], has allowed to determine the dissociation energy D_e, the exchange energy ΔV_e and the coefficients C_n of the dispersion energy ΔV_c:
$$V = D_e + \Delta V_e + \Delta V_c \text{ with}$$
$$\Delta V_e = -Ae^{-aR} \text{ and } \Delta V_c = -C_6/R^6 - C_8/R^8 ..$$
The following values were obtained [2]:
$$D_e = 4450.78\ (0.15)\ cm^{-1}$$
$$v_D = 85.27\ (6).$$

A comparison between the exchange energies derived in the present work and those calculated using predictive asymptotic surface integral methods [3] is presented on the figure below:
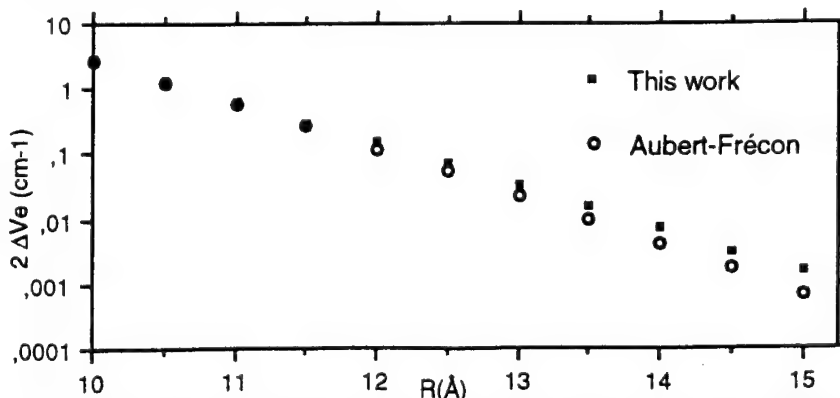
[1] R. J. LeRoy, Chemical Physics Report, CP 425, University of Waterloo (1992).
[2] C. Amiot, J. Vergès and C.E. Fellows, submitted to J. Chem. Phys.
[3] M. Aubert-Frécon, personnal communication. G. and G. Hadinger and M. Aubert-Frécon, J. Mol. Spectrosc. (to appear).

Q5

USE OF LENNARD-JONES-POTENTIALS FOR VAN DER WAALS INTERACTION

D. Zimmermann

Institut für Strahlungs- und Kernpyhsik

Technische Universität Berlin

Hardenbergstr. 36, D-10623 Berlin

Lennard-Jones (12, 6) or (8, 6) potentials have frequently been used in the past as a simple representation of the van der Waals interaction between two atoms. The two parameters of the LJ function C_n/R^n - C_6/R^6 with $n = 12$ or 8 are completely determined if two spectroscopic parameters, e.g. ν_e and B_e, are known from experiment. In this case, all other Dunham coefficients may be expressed in terms of ν_e and B_e. As an example we use the Dunham coefficient $Y_{20} = -x_e\nu_e$ of vibration. By means of a simple calculation one obtains the relation $x_e = kB_e/\nu_e$ with $k = 45.5$ for (12, 6) and $k = 29.83$ for (8, 6). If on the other side ν_e, B_e and x_e are known from experiment, one can select the proper form of the LJ function by means of the experimental value of k. For the $A^2\Pi$ state of the van der Waals molecule NaKr, for instance, k turned out to be 31.5 /1/, thus explaining why a slightly modified LJ (8, 6) function turned out to be a suitable analytical representation of the interatomic potential of this electronic state.

/1/ R. Brühl et al., J. Chem. Phys. 94 (1991) 5865

Q6

HIGH RESOLUTION LASER SPECTROSCOPY ON THE $S_1 \leftarrow S_0 6_0^1$ VIBRONIC BAND OF BENZENE AND INTERPRETATION OF THE OBSERVED SPECTRUM

M. Okruss, R. Müller and A. Hese

Institut für Strahlungs- und Kernpyhsik
Technische Universität Berlin
Hardenbergstr. 36, D-10623 Berlin

This work deals with (i) the experimental setup for efficient second harmonic generation of cw laser radiation at 259 nm and (ii) its application to the analysis of the $(^1B_{2u} \leftarrow {}^1A_{1g})\ 6_0^1$ rotational structure of benzene. The output power of a commercial cw ring dye laser (Coherent CR 699) operating with Coumarin 6 was coupled into an external ring resonator for frequency doubling [1]. With an input power of 200 mW it was possible to achieve 4.2 mW of UV-power at 259 nm by using a 40 mm long KDP-crystal. This narrow band laser radiation was crossed at right angle with a collimated molecular beam of argon seeded with benzene. More than 300 GHz of the spectrum with $\approx$ 800 rotational transitions were recorded and analyzed. In the excited state, apart from rotational constants, first order coriolis coupling (ζ_v), centrifugal distortion (D_J, D_{JK}, D_K), centrifugal distortion corrections to the first order coriolis term (η_J, η_K) and the q-term were considered. Fitting of the rotational constants and the above mentioned terms resulted in a standard deviation of only 5.2 MHz.

[1] M. Brieger, A. Hese, A. Renn, et al., Opt. Comm. 38, 423 (1981)

Q7

LASERSPECTROSCOPY ON PENTACENE MOLECULES
IN A SUPERSONIC JET

E. Heinecke, D. Hartmann, R. Müller und A. Hese

Institut für Strahlungs- und Kernpyhsik
Technische Universität Berlin
Hardenbergstr. 36, D-10623 Berlin

We investigated the rotational structure of the vibrationless $S_1 \leftarrow S_0$ transition of pentacene at 18649.003(2) cm^{-1} by high resolution laser spectroscopy. Pentacene was seeded and cooled in a supersonic argon jet. The excitation was done by laserlight produced by a tunable ring dye laser and integrated fluorescence was detected by a photomultiplier. The resulting spectrum has a high line density, caused by the large size of the molecule. In computer calculations with ASYROT [1], we determined the rotational constants of pentacene considered to be planar in the ground and first excited state:

A" = 1320.6(9) MHz $\Delta A = A'-A'' = 13.2(3)$ MHz

B" = 117.97(9) MHz $\Delta B = B'-B'' = -0.76(5)$ MHz

C" = 108.28(15) MHz $\Delta C = C'-C'' = -0.54(6)$ MHz

In earlier measurements the vibronic spectrum of the $S_1 \leftarrow S_0$ transition was resolved and identified [2]. The reported band origin had to be corrected by +21 cm^{-1}. Because pentacene is one of the most important molecules in the new exciting field of single molecule spectroscopy [3], it is important to get more information about the free molecule.

[1] F.W. Briss et.al., Computer Phys. Com. 38,83 (1984)

[2] A. Amiravet al., Chem. Phys. Lett. 72, 1, 21 (1980)

[3] M. Orrit and J. Bernard, Modern Phys. Let. B 5, 11, (1991)

Q8

A possible identification of the FeH_2 radical from its infrared spectrum

H. Körsgen, P. Mürtz, K. Lipus, J.P. Towle*, J.M. Brown*, W. Urban

Institut für Angewandte Physik, Universität Bonn
Wegelerstr. 8, D-53115 Bonn, Germany

* Physical Chemistry Laboratory
South Parks Road, Oxford OX1 3QZ, England

We present spectra of several infrared ro-vibrational transitions around 1675 cm^{-1} which indicate that the detected molecule is FeH_2. This would be the first detection of the free FeH_2 radical in the gas phase. The spectra were recorded with a Faraday laser magnetic resonance (LMR) spectrometer utilizing a CO laser. The radical was produced in an electric d.c. glow discharge of normal type with $Fe(CO)_5$ and hydrogen using helium as carrier gas. The analysis of the spectrum is performed with the method of the effective Hamiltonian expressed in a Hund's case (a) basis set.

The only experimental information about the FeH_2 radical has been obtained by measurements in rare gas matrices using the photochemical Fe + H_2 reaction [1,2]. The geometry of the ground state has been calculated to be linear ($^5\Delta_g$) from ab initio calculations. In this case, the symmetric stretching band is not infrared active. Therefore, we assign the detected signals to the antisymmetric stretching fundamental band. The matrix isolation study in an Ar matrix suggests that the vibrational interval is 1661 cm^{-1}.

[1] G.A. Ozin, J.G. McCaffrey, J. Phys. Chem. 88, 645 (1984)
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EFFECTIVE ROTATION -PSEUDOROTATION HAMILTONIAN FOR X_3-TYPE MOLECULES AND TRIAL ANALYSIS OF B-X BAND SPECTRUM OF Na_3

N. Ohashi and M. Tsuura
Kanazawa University, Kanazawa, 920 Japan
J. T. Hougen
National Institute of Standards and Technology
Gaithersberg, Maryland, 20899 U.S.A.

The rotation-pseudorotation problem in X_3 -type molecules has been treated group-theoretically for the high-barrier tunneling case as the first step of this work. Explicit expressions for rotation-pseudorotation Hamiltonian matrix elements, which take into account interaction of overall rotation both with the rotation of principal axes accompanying pseudorotation motion and with the angular momentum generated by pseudorotation motion, have been derived using an m-fold extended group of the G_{12} permutation-inversion group. Illustrative pseudorotation tunneling splitting patterns have been derived by numerically diagonalizing the resulting Hamiltonian matrix. In the next stage, a more general formalism applicable to cases with low-barrier pseudorotation-tunneling has been derived group-theoretically by making use of concepts from the high-barrier treatment, and the formalism was applied to a trial global analysis and least squares fit for the u=1 low-barrier pseudorotation states in the B - X system of Na_3 reported by Ernst and Radkowsky[1,2].

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Q10

INVESTIGATION OF PREDICTIONAL ABILITIES OF DIFFERENT FORMS OF EFFECTIVE HAMILTONIANS BASED ON MOLECULAR HAMILTONIAN IN THE PRINCIPAL AXES OF INERTIA

A.Ya.Tsaune

Ukrainian State Chemical and Technological University, av.Yu.Gagarin 8,

320005 Ukraine

M.P.Dyachenko

Dnepropetrovsk State University, per. Nauchny 13, 320625

Dnepropetrovsk, Ukraine

Comparative analysis of predictional calculation results for vibration-rotation states of $H_2{}^{16}O$ molecule is carried out using the following effective hamiltonians (EH) :

♦ finite-dimensional representation on vibrational states of molecular hamiltonian (MH) in the principal axes of inertia;

♦ EH obtained from MH using perturbation theory (PT); matrix elements of the EH depend polynomially on well-known quantum numbers J,K;

♦ Pade-approximants of matrix elements of polynomial form;

♦ rolled up form of EH obtained through analytical summing of PT series.

Q11

INTERNAL MOTION EFFECTS IN THE MICROWAVE SPECTRUM OF OCS TRIMER

James P. Connelly[1], Alfred Bauder,

Laboratorium für Physikalische Chemie, E.T.H.

CH-8092 Zürich, Switzerland.

Alan Chisholm, Brian J. Howard,

Physical Chemistry Laboratory, South Parks Road,

Oxford. OX1 3QZ. U.K.

John S. Muenter,

Department of Chemistry, University of Rochester,

Rochester. New York 14627. U.S.

The microwave spectrum of OCS trimer has been measured between 6 and 18 GHz using pulsed nozzle, Fourier-transform microwave spectroscopy. The spectrum is consistent with an oblate asymmetric rotor, $\kappa = 0.18$, with a- and c-type transitions observed. Fine doubling of some of the pure rotational lines is interpreted as indicating a tunnelling motion between two chiral forms of the complex, where the splitting is the result of slightly different rotational constants associated with the symmetric and antisymmetric tunnelling states. A fit of averaged transition frequencies to Watson S reduction rotational parameters gave: $A = 847.97957(3)$, $B = 736.17579(2)$, $C = 574.32589(2)$ MHz, $D_J = 0.4544(1)$, $D_{JK} = 0.1571(6)$, $D_K = 0.3011(6)$, $d_1 = 0.06798(6)$, $d_2 = 0.0339(3)$ kHz. Postulated structures based on electrostatic interactions are obtained by relaxing the arrangement of three OCS molecules from their parallel, stacked orientation in the molecular crystal[2]. The proposed internal motion involves the tunnelling rearrangement between the two chiral forms of the complex by reversing the slipped near-parallel orientation of two OCS molecules. The results of modelling calculations will be presented.

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[1]Current address; Institut für Physikalische Chemie, Klingelbergstasse 80, CH-4056 Basel, Switzerland.

[2]L. Vegard, *Z. Krist.* **77**, 411 (1931).

Q12

ANALYSIS OF HIGH RESOLUTION INFRARED SPECTRA OF OZONE IN THE 4600 cm^{-1} REGION

S. Mikhailenko, A. Barbe, J.J. Plateaux and Vl G. Tyuterev

G.S.M.A., U.A. CNRS D 1434

Faculté des Sciences

BP 347 - 51062 REIMS Cédex - France

The spectra of ozone using high product p x ℓ have been recorded with the Fourier Transform spectrometer of Reims, with a resolution of 0.008 cm^{-1}, p = 40 Torr O_3, L = 36 m, in the 4 600 cm^{-1} region. This one corresponds mainly to the $v_1+v_2+3v_3$ band. The analysis of this band is difficult due to the presence of the two very closed interacting bands v_2+4v_3 and $3v_1+2v_2$: many transitions of these two weak bands have been observed, up to J = 50 for v_2+4v_3 and one serie corresponding to K = 3 for $3v_1+v_2$.

We have used an hamiltonian which takes explicitly account of Coriolis coupling between 113 and 014, 113 with 320 as well a Fermi resonance between 014 and 320. The set of parameters of these states, comparison O^{bs} - C^{alc} , as well as intensities are presented.

357

Q13

LINESHIFTS IN THE ν_3 BAND OF N_2O AND THE 1 $\leftarrow$ 0 BAND OF CO INDUCED BY VARIOUS PERTURBERS

F. Rachet, M. Margottin, J.-P. Bouanich, A. Henry
and A. Valentin

Laboratoire de Physique Moléculaire et Applications, C.N.R.S.,

Université P. & M. Curie, 4, Place Jussieu, Tour 13, Bte 76,

F-75252 Paris Cedex 05 FRANCE

Lineshift measurements have been performed in the N_2O ν_3 band perturbed by N_2, O_2, He, Ar and Xe and in the CO 1 $\leftarrow$ 0 band perturbed by N_2, O_2, He, Ne, Ar and Xe.

The accurate modelling of the apparatus function of our very long optical path length Fourier transform spectrometer allows to derive directly the experimental lineshift values from two successive records, at low pressure for the first one while the total pressure, for the second one, is chosen to give a pressure broadening about four times larger than the Doppler width (around 100 torr).

The accuracy of these measured lineshifts, which are rather small, is within 0.5×10^{-3} cm^{-1} atm^{-1}. The measured values compare very well with the results we obtained from our TDL spectrometer (accuracy of 0.2×10^{-3} cm^{-1} atm^{-1}) for the few lines available with this instrument.

A comparison is reported between the experimental values and calculated values based on a semi-classical model.

Q14

LINE INTENSITIES FOR THE 10μm BANDS OF $^{32}SO_2$

A.Perrin, J.-M.Flaud, C.Camy-Peyret,
Laboratoire de Physique Moléculaire et Applications,
CNRS, Université Pierre et Marie Curie,
Tour 13, bte 76,4 Place Jussieu,
F-75252 PARIS, Cedex 05. France
Ph.Arcas,
Laboratoire de Physique Moléculaire et Applications,
CNRS, Université Paris Sud, Bat 350 Centre d'Orsay,
F-91405 ORSAY, Cedex, France

Using high resolution Fourier transform spectra ($\mathcal{R}\sim 0.003$ cm^{-1}) recorded at LPMA, Orsay, it has been possible to measure individual line intensities for the ν_1 and ν_3 band of $^{32}S^{16}O_2$ in the 950-1200 cm^{-1} spectral region. These intensities were introduced in a least squares fit calculation allowing one to get the expansion of the transition moment operator of the ν_1 and ν_3 bands of SO_2. For these intensities calculations, the theoretical model takes into account the vibration-rotation interactions linking the upper levels involved in the $\{\nu_1, 2\nu_2, \nu_3\}$ interacting bands of SO_2. Finally a synthetic spectrum of the 10 μm band of $^{32}SO_2$ has been generated, using for the line intensities the dipole moment expansion determined in this work and for the line positions the parameters and the Hamiltonian matrix given in a previous analysis [J.-M.Flaud, A.Perrin, L.M.Salah, W.J.Lafferty and G.Guelachvili, J. Mol. Spectrosc. 160, 272-278 (1993)].
This calculation should be useful for an accurate retrieval of atmospheric SO_2.

Q15

Study of high temperature water vapor by Fourier transform spectroscopy of a low pressure flame and comparison with the HITEMP database.

R.Lanquetin, _C.Camy-Peyret_

Laboratoire de Physique Moléculaire et Applications, CNRS, UPR 136
Université Pierre et Marie Curie - Bte76 - Tour 13
4, Place Jussieu , 75252 PARIS cedex 05 , France.

J.Selby

Northrop Grumman Corp. Research and Development center,
Bethpage, NY11714, USA .

Fourier-Transform emission spectra of a low pressure ($\approx$ 20 hPa) premixed oxygen-methane flame have been recorded in the 1800 and 5000 cm^{-1} region at high resolution (0.02 cm^{-1} apodized). A large number of emission lines are observed for the species H_2O, CO_2, OH and CO. We have concentrated the analysis on the identification of the H_2O lines and assigned more than 6500 transitions involving highly excited rovibrational levels with quantum numbers up to J = 29 and Ka = 20. A comparison of the observed line positions and intensities has been perfomed with data calculated for the HITEMP database using the direct numerical diagonalization method (DND) .

Q16

OXYGEN ISOTOPIC SUBSTITUTION IN $FC\ell O_3$: THE PASSAGE FROM A SYMMETRIC TOP TO A QUASI-SPHERICAL TOP

F. MEGUELLATI [1], G. GRANER [1] and K. BURCZYK [2]

(1)Laboratoire de Physique Moléculaire et Applications, CNRS, Bât. 350, Campus d'Orsay,

F - 91405 ORSAY Cédex, France.

(2)Anorganische Chemie, FB 9, Universität-Gesamthochschule,

D - 42097 WUPPERTAL, Germany.

The values of the ratio $(A_0-B_0)/A_0$ are 0.0624, 0.0151 and 0.0153 for $F^{35}C\ell^{16}O_3$, $F^{35}C\ell^{18}O_3$ and $F^{37}C\ell^{18}O_3$ respectively: this shows that the molecule $FC\ell^{18}O_3$ is much closer to a spherical top than $FC\ell^{16}O_3$. It is well known that spherical top molecules have several infrared inactive fondamentals. A similar phenomenon is found concerning the ν_3 band of $FC\ell^{18}O_3$, which is quasi-inactive in infrared, its intensity is less than 1% of the intensity of ν_5. On the other hand, the study [1] of ν_3 in $F^{35}C\ell^{16}O_3$, and the present study of $F^{37}C\ell^{16}O_3$ both show a very clear structure of the ^QQ branches of ν_3. This leads to think that the isotopic substitution of oxygen changes the molecule from a symmetric top to a quasi-spherical top.

Since the ν_3 band of $FC\ell^{18}O_3$ cannot be observed directly, we have determined its parameters indirectly by two methods:

✱ The study of the $\nu_1+\nu_3-\nu_3$ hot band for the two isotopically pure $F^{35}C\ell^{18}O_3$ and $F^{37}C\ell^{18}O_3$ samples gives the values of B, D_J and D_{JK} for the $\nu_3=1$ state by using lower state combination differences. The s.d. on these LSCD is about 0.12×10^{-3} cm^{-1}.

✱ By analysing separately the $\nu_1+\nu_3$ and $\nu_1+\nu_3-\nu_3$ bands, we can deduce by difference of their upper state parameters all molecular parameters of ν_3.

A further check of the parameters obtained can be made by a comparison with the differences of the parameters of $\nu_1+\nu_3$ and ν_1, which should be very similar.

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Q17

OPTICAL-OPTICAL DOUBLE RESOUNANCE

POLARIZATION SPECTROSCOPY

OF THE $(1)^1\Pi$ STATE AND $(2)^1\Pi$ STATE OF KRb

N.Okada, S.Kasahara, and H.Katô

Department of Chemistry, Faculty of Science, Kobe University,

Nada-ku, Kobe 657, Japan

The $(1)^1\Pi$ and $(2)^1\Pi$ states of the KRb molecule have been observed for the first time using the technique of Doppler-free optical-optical double resounance polarization spectroscopy. Molecular constants of the $(1)^1\Pi$ and $(2)^1\Pi$ states of the KRb molecule were determined. A number of rovibrational levels are found to be strongly perturbed. The energy shifts of the e and f levels are studied, and the perturbations between the $^1\Pi$ and $^3\Sigma^+$ states and between the $^1\Pi$ and $^3\Pi$ states are identified. Irregular variations of molecular constants of both the $(1)^1\Pi$ and $(2)^1\Pi$ states which are attributed to their electrostatic perturbation were observed.

Q18

MILLIMETER WAVE SPECTRUM OF As^{35}Cl$_3$ OBSERVATION OF K=3 LINE SPLITTING AND DETERMINATION OF ARSENIC AND CHLORINE HYPERFINE PARAMETERS

G. Cazzoli, G. Cotti, C. Degli Esposti, and **L. Dore**
Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi, 2
I 40126 Bologna, Italy

J.M. Colmont
Laboratoire de Spectrosopie Hertzienne, URA CNRS 249, Bât. P5
Université del Lille I
F 59655, Villeneuve d'Ascq Cedex, France

The ground state rotational spectrum of arsenic trichloride has been recorded between 120 and 376 GHz allowing the determination of the sextic and one octic centrifugal distortion constants. Among the sextic constants, the h_3 one, responsible for the A$_1$/A$_2$ splitting of the K=3 lines, has been determined following the observation of the splitting in the transitions with $J \geq 50$.

Even in the high J transitions, the high K lines split in two components because the arsenic nuclear quadrupole coupling. The recording of several of such hyperfine components allowed the refinement of the value of the quadrupole constant. In addition, Lamb Dip spectra were obtained for the J=42 $\leftarrow$ 41, K=0-6 transitions: the accuracy of a few kHz in the frequency of the hyperfine components allowed the determination of the arsenic C$_N$ spin rotation constant.

Finally, the observation of an additional splitting in the J=25 $\leftarrow$ 24, K=11-13 transitions, due to the plural quadrupole coupling of the chlorine atoms, allowed us to determine the quadrupole constants for such atoms.

Q19

FERMI RESONACES AND LOCAL MODES IN STIBINE: SbH_3. FOURIER INTERFEROMETRIC AND LASER PHOTOACOUSTIC OVERTONE SPECTRA

Juha Lummila, Tuomas Lukka, and Lauri Halonen

Laboratory of Physical Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1),

FIN-00014 University of Helsinki, Finland

Hans Bürger

FB9-Anorganische Chemie, Universität Gesamthochschule, D-42097

Wuppertal, Germany

The third stretching overtone region of a natural sample of stibine, SbH_3, has been studied with high resolution infrared spectroscopy and the fifth and the sixth overtone region with Ti:Sapphire ring laser intracavity photoacoustic spectroscopy. The third overtone consists of a local mode pair of bands $(400A_1/E)$ which have been rotationally assigned both for $^{121}SbH_3$ and $^{123}SbH_3$ with a standard vibration-rotation model based on rectilinear normal coordinates. The vibrational dependencies of the model parameters are explained well with a simple block diagonal vibrational model. An extension of the standard vibration-rotation model is used to show that the upper state rotational energy level structures of both isotopic species are close to the rotational structure of an asymmetric rotor. High resolution laser spectrum of the fifth overtone consisting of a local mode pair of bands $(600A_1/E)$ shows severe pertubations in the upper state rotational structure. The $(510A_1/E)$ and $(700A_1/E)$ bands have been recorded with low resolution. All experimentally known vibration-rotation bands of $^{121}SbH_3$ have been reproduced well with a curvilinear internal valence coordinate system based Fermi resonance - local mode model. The potential energy surface obtained agrees well with recent *ab initio* results.

Q20

The Coriolis Resonating Triad ν_4/ν_{10}/ν_{11} of CH_3CD_3

G. Nivellini, F. Tullini, and L. Fusina

Dipartimento di Chimica Fisica e Inorganica, Università di Bologna
Viale Risorgimento 4, 40136 Bologna, Italy

In the range 950-1200 cm^{-1} of the infrared spectrum of $^{12}CH_3{}^{12}CD_3$ a large number of vibration-rotation transitions, which can be assigned to $\nu_4(A_1)$, ν_{10} (E) and ν_{11} (E), is present. These bands can Coriolis interact with each other and while ν_{11} can be identified with confidence, ν_4 and ν_{10} appear heavily perturbed and are assigned with greater difficulty. The simultaneous analysis of the three bands, based on a model which includes Coriolis interactions among all the considered excited states, has now been completed. Using 632 transitions assigned to ν_4 , 914 transitions assigned to ν_{10} and 2965 transitions (519 of which are 'forbidden') assigned to ν_{11} , we have been able to determine most of the interaction parameters.

Ground state combination differences obtained from these bands, toghether with those from ν_2 , and microwave rotational transitions, provided accurate values of the ground state parameters, including A and D_k, which cannot be obtained from the analysis of the $\Delta_k = 0$ allowed transitions only.

Q21

REGULAR AND OSCILLATORY PARTS
OF THE DENSITY OF STATES:
GENERATING FUNCTION APPROACH

D.A. Sadovskii, <u>B.I. Zhilinskii</u>

Université du Littoral, Dunkerque, 59279, France

Simple analytical formulae for the smooth regular part and for the oscillatory part (fluctuations) of the density of states as a function of energy are derived. These formulae are derived from the generating functions that account for resonances between the vibrational modes and for the symmetry of the problem, so that the density of states of a particular symmetry type can be computed. Examples of the vibrational structure of triatomic molecules A_3, tetrahedral molecules AB_4, and linear molecules AB_2 are considered. The analytical formulae are compared with the *ab initio* results for H_3^+ ion [J. R. Henderson *et al.*, J. Chem. Phys. **98**, 7191 (1993)] (see figure below).
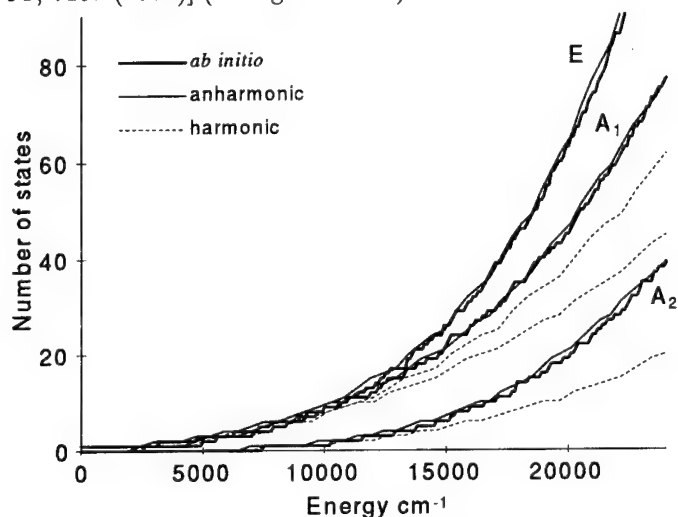
As an example we present integral densities of vibrational states of different symmetry types versus energy for the H_3^+ ion. Densities in the harmonic approximation, anharmonicity corrected densities, and *ab initio* densities are shown.

Q22

FAR INFRARED EMISSION FROM STRATOSPHERIC
HYDROGEN PEROXIDE

B. Rebours

Laboratoire de Géophysique Externe,
Université de Rennes, 22302 Lannion, France

Synthetic emission spectra from two stratospheric altitude observations have been analyzed for the presence of H_2O_2 in the far infrared region. The calculations are made with a high spectral resolution greater than those in experimental measurements which are in the region of 3.10^{-3} cm^{-1}. Spectra cover a spectral interval between 40 and 120 cm^{-1} showing the best features of H_2O_2 susceptible to observation in a stratospheric spectrum. Using the variations in H_2O_2 abundance in the measurement data and photochemical models, the H_2O_2 features detection limits have been studied. Results show that the individual spectral lines of the R branch can be detected in the stratosphere with an instrument of better resolution than those used actually. Both, the $^RQ_4$ and $^RQ_5$ branches are detectable in a spectrum of the middle stratosphere with a resolution of the instruments close to 3.10^{-3} cm^{-1}. At present, with this resolution of the instruments, the $^RQ_4$ branch and especially the $^RQ_5$ branch are the only features of H_2O_2 liable to restore a concentration of this constituent in an altitude zone limited to the middle stratosphere.

Q23

ROVIBRATIONAL ANALYSIS OF CYANOACETYLENE (HCCCN) ON THE BASIS OF MILLIMETER, INFRARED AND STARK SPECTRA

L. Mbosei, B. Coveliers and **A. Fayt**
Université Catholique de Louvain, Chemin du Cyclotron 2 B-1348 Louvain-la-Neuve, Belgique

E. Arié and **G. Graner**
L.P.M.A., CNRS, Bât. 350 Campus d'Orsay
F91405 Orsay Cedex, France

J. Cosléou and **J. Demaison**
Lab. de Spectroscopie Hertzienne CNRS, Univ. des Sciences et Technologies de Lille
F-59655 Villeneuve d'Ascq Cedex, France

The millimeter-wave spectrum of HCCCN has been studied in the regions 148-159, 227-240, 299-302, 347-358, and 436-467 GHz. More than 1000 lines have been measured and most of them have been assigned. The weakest lines belong to vibrational states as high as 1900 cm^{-1}.

The F.T. infrared spectrum of the ν_5, ν_6 and $\nu_6 + \nu_7$ bands of HCCCN have been reinvestigated with the help of the global analysis. We complete the 24 already published bands[1] by 72 newly assigned ones. We so reach vibrational levels up to 1600 cm^{-1}.

The CO laser saturation Stark spectrum of the $2\nu_5$ band has been completed and concerns upper states in the range 1300-2210 cm^{-1}.

A global analysis has been applied to all data. In this analysis we automatically construct the energy matrices with rotational and vibrational ℓ-type and anharmonic off-diagonal terms. We determine more than 200 molecular parameters which roughtly reproduce all experimental data.

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Q24

HIGH RESOLUTION INFRARED SPECTRUM AND ANALYSIS OF THE ν_9 BAND OF $CH_2{=}CHF$

Alberto Gambi

Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine

Via Cotonificio 108, I-33100 UDINE (Italy)

The infrared spectrum of vinyl fluoride has been recorded in the region 350–770 cm^{-1} with a resolution better than 0.002 cm^{-1} employing the Bruker IFS 120 HR vacuum Michelson interferometer at the Giessen University.

The $CH_2{=}CHF$ molecule is án asymmetric top rotor ($\kappa = -0.945$) which belongs to the symmetry point group C_s. The ν_9 fundamental centered at 483.07 cm^{-1} can be approximately described as the C=C–F in-plane bending, it is of symmetry species A' and the expected ab-type band envelope shows a prevalent contribution of the b-type component.

A detailed investigation of the rovibrational structure has been carried out involving a- and b-type band selection rules, relative intensity calculations and combination differences. Using Watson's A-reduction Hamiltonian in the I^r representatiom, a least-squares fit of about 3000 assigned transitions led to the determination of a reliable set of rotational and centrifugal distortion parameters for the first excited vibrational level.

Spectra, details of the interpretation and results obtained from the analysis will be presented.

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Q25

Diode Laser Spectroscopy of Chlorofluoromethane
in the 9-10 μm Region.

A. Baldacci and P. Stoppa

Dipartimento di Chimica Fisica, Università di Venezia
D.D. 2137, I-30123 Venezia, Italy

High-resolution spectra of natural CH_2FCl have been recorded at 240 K between 1040-1120 cm^{-1} and 985-1013 cm^{-1} using a tunable diode laser.

The two spectral regions are characterized by the absorptions of the C-F stretching mode v_4 (A') at 1067.8 cm^{-1} and the CH_2 rocking vibration v_9 (A") at 1002.3 cm^{-1}.

Chlorofluoromethane is an asymmetric top of C_s symmetry with nine normal modes and an asymmetry parameter $\kappa = -0.972$. The v_4 fundamental is an hybrid band consisting of both a- and b-type transitions with a larger contribution of the former one. Aside the asymmetry splitting ($K_a \leq 6$), the band shows a structure very similar to a parallel (a-type) and a perpendicular (b-type) band of prolate symmetric tops. Assignment has been extended up to J = 55 and K_a = 17 for the ^{35}Cl isotopomer. The v_4 level interacts with v_9 through first order a-, b-Coriolis resonance and the observed irregularities in the $K_a' = 13$ sublevel have been ascribed to higher order a-type Coriolis coupling; this effect is clearly evident near the crossing which happens at J' = 34.

The v_9 band, severely overlapped in the R-branch by the stronger P-branch of v_4, should give rise to a pure c-type band. However the expected lines ($\Delta K_a = \pm 1$, $\Delta K_c = 0$) are very weak while the stronger transitions have different selection rules $\Delta K_a = 0$ and $\Delta K_c = 0$. This behaviour is due to the Coriolis perturbation with v_4. The rovibrational transitions in the P-, Q- and R-branch regions led to the assignment of lines up to J = 42, and $4 \leq K_a \leq 17$ for the ^{35}Cl species.

Due to the high density of the spectral lines, assignment concerning to the less abundant ^{37}Cl species presented some difficulties. In order to produce a consistent set of constants, we have synthesized the pure monoisotopic ^{37}Cl species; the spectra have been already measured in the v_4 band region and the analysis is currently in progress.

Details of the interpretation and results from the analysis will be reported.

Q26

ANALYSIS OF THE LMR SPECTRA OF CH_2Br

Y. Liu, Z. Liu and P. B. Davies
Department of Chemistry, University of Cambridge,
Cambridge CB2 1EW, UK.

Bromine has been estimated to be approximately 40-100 times more effective than chlorine, on an atom-per-atom basis, in destroying stratospheric ozone at the current levels of stratospheric chlorine. The major source of stratospheric bromine is methyl bromide (CH_3Br), believed to have both natural and anthropogenic sources. The major known atmospheric removal process for CH_3Br is its reaction with OH radicals to form the CH_2Br radical and H_2O. The far infrared laser magnetic resonance spectra of the CH_2F and CH_2Cl free radicals, the F and Cl analogues of CH_2Br, have already been detected. For several reasons they have very complex Zeeman spectral patterns which have not been analysed. The FIR LMR on CH_2Br has also been carried out in Cambridge and similarly complex structures were obtained for CH_2Br spectra. A procedure has been developed to explain and analyse the LMR spectra of these radicals. Excellent agreement between the experimental spectra of CH_2Cl and the simulation was achieved. And qualitative agreement between the experimental and simulated spectra of CH_2Br was also obtained. It is therefore believed that the complete analysis of the LMR spectra of CH_2Br will be possible when the frequency measurement on the laser lines, which gave the simplest pattern of the LMR spectra of CH_2Br, is available.

Q27

High Resolution FTIR-Spectra of the Perpendicular Fundamental ν_8 of Trideutero-Triazine

R. Ruber, B. Macht and A. Ruoff,

Sektion Schwingungsspektroskopie,
Universität Ulm,
Albert-Einstein-Allee 11
89081 Ulm, Germany

The High Resolution Fourier-Transform-Spectra of $C_3N_3D_3$ (Group $D_{3h}(M)$) has been recorded with the Bruker 120 HR interferometer at Gießen with a resolution of about 0.0018 cm^{-1} at room temperature.

About 1000 lines of ν_8, located at 1275 cm^{-1}, have been measured and assigned. The ground state constants up to the H's have unambiguously been deduced previously being derived from about 5400 GSCD's of the two parallel fundamentals ν_{11} and ν_{12} and two perpendicular fundamentals ν_9 and ν_{10}. The standard deviation of the latter is about 200 μK. The excited state constants up to the H's will be presented, too and a strong resonance with an yet unidentified perturber will be discussed.

Q28

THE ROTATIONAL STARK EFFECT OF PROPYNYL ISOCYANIDE

J. Gripp, U. Kretschmer, and W. Stahl

Inst. für Physikalische Chemie, Christian-Albrechts-Universität Kiel,
D-24098 Kiel, Germany

D. Lentz, B. Meisner, N.Nickelt,
and D. Preugschat

Inst. für Analytische und Anorganische Chemie,
Freie Universität Berlin,
D-14195 Berlin, Germany

In 1993 we began the investigation of the rotational spectrum of propynyl isocyanide, CH_3C_2NC, a molecule of astrochemical interest. Similar to isocyanoacetylene, HC_2NC, the preparation had been carried out by vacuum pyrolysis of a chromium carbonyl complex, in this case pentacarbonyl-(1,2-dichloro-1-isocyano-propenyl)-chromium, $(CO)_5Cr-CN-C(Cl)=C(Cl)-CH_3$. Because CH_3C_2NC decomposes rapidly in a brass waveguide sample cell normally used for Stark modulation microwave spectroscopy, an investigation of the rotational Stark effect and subsequently a determination of the molecular electric dipole moment was not possible.

Now we present an investigation of the rotational Stark effect of CH_3C_2NC with a molecular beam Fourier transform microwave spectrometer equipped with electrodes for the generation of an additional static electric field. The obtained value for the electric dipole moment is in good agreement with one predicted by an ab initio calculation *. Comparisons with related molecules will be given.

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50th Int. Meeting of Physical Chemistry
Mont Sainte-Odile, France Sept. 1993

Q29

SUB-DOPPLER ZEEMAN SPECTROSCOPY OF THE S_1 B_{3u} - S_0 A_{1g} 0^0_0 BAND OF PYRAZINE

Masaaki Baba

Faculty of Integrated Human Studies,
Kyoto University, Kyoto 606, Japan

Norimasa Yamamoto and Tsuyoshi Ebi
Department of Chemistry, Faculty of Science,
Kobe University, Kobe 657, Japan

It is known that fluorescence of pyrazine is remarkably quenched by the external magnetic field due to the enhancement of radiationless transitions. In order to understand this effect clearly, high-resolution (15 MHz) fluorescence excitation spectrum and the change with the magnetic field have been observed for the S_1 B_{3u} - S_0 A_{1g} 0^0_0 band of pyrazine in a collimated molecular beam. At zero field, a number of lines are observed for each rotational transition because of strong interaction with the triplet levels.

For $J = 0$ level, it was found that most of these lines were shifted or by the magnetic field. The spectral feature could be approximately reproduced by the calculations in which we considered the mixing of spin sublevels. For $J \neq 0$ levels, several lines were split and the intesities were appreciably decreased in the weak magnetic field. This magnetic field effect is interpreted by the Zeeman splitting in coupling triplet levels. Consequently, the radiationless transitions and magnetic fluorescence quenching of pyrazine were attributed primarily to the singlet-triplet interaction and the Zeeman effects in the triplet state.

Q30

Global Fit of Torsional-Rotational Transitions in the ν_t = 0 and 1 Torsional States of Methanol

Li-Hong Xu[*] and Jon T. Hougen

Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

(* *NIST Guest Researcher 1994 - 1995. Permanent address: Physical Sciences Department, University of New Brunswick, Saint John, N.B., Canada E2L 4L5)*

Methanol data for ν_t = 0 (below the barrier) and ν_t = 1 (straddling the barrier) have been treated, using a program based on the formalism of Herbst *et al.* [1]. All together, 906 microwave lines (mostly assigned a 50 kHz measurement uncertainty) and 197 tunable far-infrared lines (mostly assigned 100 or 200 kHz uncertainties) in the range $K \le 12$, $J \le 20$ and 5549 Fourier-transform far-infrared lines (assigned a 0.0002 cm^{-1} = 6 MHz uncertainty) in the range $K \le 14$, $J \le 20$ have been globally fit to give a unitless weighted standard deviation of 1.032, using 56 adjustable and 8 fixed parameters. Some difficulties remain in fitting high K and J $\underline{b}$-type tunable far-infrared lines. Although these difficulties may arise from deficiencies in the model, it also seems possible that some measurement problems still remain in the tunable far infrared data set. Apart from the high K and J difficulties with this latter data set, a very satisfactory fit has been achieved, leading us to the conclusion that up through the first excited torsional level, a traditional one-dimensional internal rotation model is capable of accurately describing methanol energy levels, without consideration of other large-amplitude-motion effects, such as those arising, for example, when the OH bending vibration carries the molecule to a C_{3v} configuration and the internal rotation barrrier vanishes.

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Q31

IR LINESHIFT MEASUREMENTS IN THE V=2←V=0 BAND OF CO PERTURBED BY He, Kr, N_2 AND O_2.

J.L. Domenech, D. Bermejo, R. Martínez and J. Santos
Instituto de Estructura de la Materia, C.S.I.C.,
C/ Serrano 123 Madrid SPAIN
J.-P. Bouanich and C. Boulet
Laboratoire de Physique Moléculaire et Applications, C.N.R.S., Université
Paris-Sud, Bâtiment 350, Orsay, FRANCE.

The pressure-induced lineshift of 17 rovibrational lines in the P and R branches of CO $v=2 \leftarrow v=0$ Band has been measured with the High Resolution Difference Frequency IR Laser Spectrometer of Madrid[1] , that provides an instrumental resolution of 3 MHz.

Self-perturbation and perturbation by four foreign gases, He, Kr, N_2 and O_2 has been measured for lines R(J) with J=0,1,2 and higher odd values up to J=21, and P(J) with J=1,2,3,5,7, in the pressure range of 0.-1. Bar.

In order to enhance the accuracy in the measurement of the small shifts, a dual beam configuration has been used, with the reference beam monitoring the absorption of a cell filled with pure CO at low pressure. A temperature-stabilized etalon -150 MHz FSR, 1 MHz linewidth- provided for the relative calibration. The FSR was previously calibrated against IR standards with a precision of $5. \times 10^{-5}$.

The overall accuracy of the measured shift parameters is estimated to be of about 10^{-4} cm-1. The shift shows a linear dependence upon the total pressure, the residuals being consistent with this error estimation.

A Theoretical analysis of these results is in progress.

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Q32

RESONANCE EFFECTS IN MOLECULAR SPECTRA COLLISION BROADENING AND SHIFT

A.I.Nadezhdinskii

General Physics Institute, Russian Academy of Sciences,
Moscow, Russia

Tunable Diode Laser spectrometer was used to obtain spectra of H_2O and SF_6 considering as model objects. When collision effects are considered, two energy level model is valid for H_2O spectral line under investigation, while equal distance energy scheme is a good approach to describe energy level structure of spherical top molecule SF_6. Collision broadening and shift were investigated when using different buffer gases (noble gases for H_2O, noble gases, CO, N_2, H_2, $^{34}SF_6$ for $^{32}SF_6$). Normalized collision shift of H_2O line demonstrates sharp rise when its dependence vs adiabatic parameter is considered. Pronounce resonance in vicinity of adiabatic parameter equal one was observed for SF_6 collision broadening crossection. Model was proposed to explain observed resonance. The model takes into account energy crossing of colliding molecule system when relative translation motion is treated in quantum manner. Good agreement between experimental data and model calculation was observed without any adjustment parameter in model calculations.

Q33

Self-, air, nitrogen and noble gas broadening
in the ν_1 and ν_3 bands of H_2S

I. Meusel, B. Sumpf[*], H.-D. Kronfeldt

Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1

Straße des 17. Juni 135, 10623 Berlin, Germany

e-mail: trevor@marie.physik.tu-berlin.de

The present paper reports measurements concerning broadening coefficients of absorption lines in the weak ν_1 and ν_3 bands of H_2S in the wavenumber region between 2690 cm^{-1} and 2765 cm^{-1}. The studies were carried out applying a tunable diode laser spectrometer including 17 lines of the ν_1 band with $3 \leq J" \leq 17$, $0 \leq K_a" \leq 6$ and 5 lines of the ν_3 band with $3 \leq J" \leq 5$, $1 \leq K_a" \leq 7$. We were able to measure these weak lines by implementing a Herriott multipass cell with a pathlength of about 5 m. As perturbers we chose H_2S, N_2, air, He, Ne, Ar, Kr, and Xe.

We discuss the dependence of the broadening coefficient γ on $J"$ and $K_a"$ and on the different interactions between absorber and perturber (H_2S - H_2S: dipole - dipole interaction; H_2S - N_2, air: dipole-quadrupole interaction; and H_2S - noble gases: dipole - induced dipole interaction). The observed effects will be compared with data from the ν_2 band of H_2S and results in the ν_1 and ν_3 bands of SO_2, where only weak intramolecular interactions occur.

Q34

Line shapes investigated by coherent transient experiments: narrowing and asymetry induced by the speed dependence of relaxation rates

F. ROHART and F. KAGHAT

Laboratoire de Spectroscopie Hertzienne, U.A. C.N.R.S. 249,
Université de Lille 1, 59655 Villeneuve d'Ascq Cedex.

For the interpretation of molecular collision processes, simpler models consider that the coherence relaxation induced by collisions on gaseous samples is purely exponential. The related broadening mechanism corresponds to a Lorentzian line shape which combines to the Doppler broadening to give a Voigt profile. Actually, such models neglect the dependence of collision induced relaxation rates and line shifts on the relative speed of collision partners, an effect which results in a narrowing and an asymetry of line shapes.

In this work, the dependence of collisional processes on molecular speeds have been studied by coherent transient experiments. The phenomenological model [1] used to describe such a speed dependence leads to a quite simple analytical expression for time-domain transient signals which are the Fourier transform of corresponding frequency-domain line shapes.

The experiments were carried out in the mm wavelength range for the $J=0 \rightarrow 1$ rotational transition of $HC^{15}N$ using a Stark switched Fourier transform spectrometer. The temperature influence on the observed relaxation rates was systematically studied in the 135-300 Kelvin range.

These investigations give a clear evidence of the departures from the Voigt line profile : the line narrowings and asymetries observed are correlated with the mass ratio of collision partners and depend strongly on the kind of intermolecular interaction involved.

From a careful examination of the temperature dependence of experimental results, combined with theoretical calculations of the speed dependence of relaxation in the frame of the Anderson-Tsao-Curnutte-Frost theory, we show that:
- in case of collisions with rare gas atoms or with diatomic molecules, observed line narrowings result simultaneously from a speed dependence of relaxation and, at a least extend, from velocity changing collisions.
- in case of collisions with polar molecules, observed line asymetries are qualitatively well explained by a speed dependence of pressure induced line shifts.

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Q35

Sub-Doppler Line Shapes and Self-Induced Pressure Effects of
Calibration Gases CO and OCS at Very Low Pressure

M. H. Wappelhorst, P. Palm, M. Mürtz, W. Urban

*Institut für Angewandte Physik
der Universität Bonn,
Wegelerstr. 8, D-53115 Bonn, Germany*

We report line shapes of molecular saturation signals of rovibrational transitions in the CO fundamental and OCS 10^00-00^00 band. Saturation line shapes are recorded for very low pressures between 0.1 and 5 Pascal. Results for self-induced low pressure effects (line broadening and shifting) are presented, extending our work on secondary frequency standards around 60 THz [1].

By use of a frequency offset-locking (FOL) scheme we stabilized the CO laser frequency to combination frequencies of our CO_2 reference lasers, which are stabilized to saturated fluorescence signals. Thus discrete CO laser transitions of our spectrometer can be tuned linearly with absolute frequency control within some 10 MHz. In a computer-controlled experiment we recorded complete saturation line shapes of molecular absorptions with absolute frequency accuracy.

The frequency stability of the offset-locked CO laser at 62,5 THz lies within 2 kHz relative to the CO_2 reference lasers (frequency stability $< 10^{-11}$ for $10\,s < \tau < 2000s$) leading to an overall absolute accuracy $\Delta v/v$ of the spectroscopy laser of better than 10^{-10}. Fast feedback to the CO laser reduces the linewidth of the beat signal between all three lasers by an order of magnitude. The linewidth of the spectroscopy laser is basically limited by the technical linewidth of the CO_2 combination frequencies (≈ 60 kHz). Consequently, the Bonn CO laser heterodyne saturation spectrometer is the most precise and accurate spectrometer in the mid-IR region around 5 µm.

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Q36

THE NO DIMER. II - ANALYSIS OF THE ν_1 BAND.

A. Dkhissi[*], A. Perrin[**] and N. Lacome[*]

[*]Laboratoire de Spectrochimie Moléculaire, URA CNRS 508, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris cedex 05, France

[**]Laboratoire de Physique Moléculaire et Applications, UPR CNRS 136, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris cedex 05, France

Spectra of the ν_1 band of $(NO)_2$ centered at 1868 cm^{-1} were recorded under a resolution of 0.008 cm^{-1} with the FTIR spectrometer. Various pressures ranging from 9 to 20 mbar were used at a constant temperature of 128 K.

Frequencies, intensities and widths of lines of the dimer were determined from a fit of the recorded profile of each individual line to a Voigt profile convolved with the apparatus function.

Measured wavenumbers up to $J = 37$ and $K_a = 16$ allowed the calculation of the rotational constants of the upper state as well as the centrifugal distorsion parameters of both ground and excited states.

From the strengths of 33 well-isolated lines the value of the transition moment was adjusted. It was found to be equal to 0,029 Debye.

Finally, the NO-broadened widths of $(NO)_2$ were estimated at 128 K.

Q37

INTRAMOLECULAR VIBRATIONS OF THE PHENOL DIMER REVEALED BY SPECTRAL HOLE BURNING (SHB) AND DISPERSED FLUORESCENCE SPECTROSCOPY

MICHAEL SCHMITT, UWE. HENRICHS, HANS. MÜLLER,
KARL KLEINERMANNS

In the hydrogen bridge bonded phenol dimer one phenol moiety is the proton donor, while the other acts as proton acceptor. The donor absorbs at longer, the acceptor at shorter wavelength than the monomer. We performed hole burning spectroscopy to rule out the existence of different conformers, absorbing in the investigated region. Holes burned in the population of the dimer are analyzed via fluorescence from the donor origin. Even acceptor vibrations could be analyzed this way, because acceptor and donor moiety belong to **one** species in the electronic ground state and share a common set of ground state levels. This is favorable, because the excited donor phenol fluoresces much more efficiently than the acceptor part. 10 low frequency modes of the donor and 8 of the acceptor moiety could be observed.

In order to assign the low frequency vibrational bands to distinct normal modes dispersed fluorescence spectra have been taken, by pumping **all** intermolecular vibrations. The Franck-Condon pattern then allows to assign unambiguously which level in the electronic ground state belongs to which excited state level. By comparison with the results of ab initio based normal mode analysis an unambigious assignment of the low frequency bands to distinct intermolecular vibrational modes can be given.

Q38

Fourier Transform Microwave Spectra
of Acetanhydride
in a Pulsed Nozzle Molecular Beam

JOHN C. GRECU, JOCHEN SEBBACH, AND ALFRED BAUDER

*Laboratory of Physical Chemistry, Swiss Federal Institute of
Technology, Universitätstrasse 22, CH-8092 Zurich, Switzerland*

Molecules containing two methyl groups ("two-top molecules") have been investigated by microwave (MW) spectroscopy for many years. In the late 1970's our group investigated methyl acetate[1] and trans N-methylethylidene imine[2] by pure rotational Stark-modulated MW spectroscopy. The frames of these two molecules were found to be planar.

Now we focussed on acetanhydride, a two-top molecule containing a frame with two possible torsional motions. We selected acetanhydride in order to continue our previous investigations on structure and dynamics of the anhydrides, R_1–CO–O–CO–R_2 with $R_1=R_2=H$[3] and $R_1=H$, $R_2=CH_3$[4]. The frames CO–O–CO of these anhydrides are planar, too.

In the Stark-modulated, room temperature MW spectra of acetanhydride no transitions have previously been observed. Therefore we decided to record its Fourier transform MW spectra of a pulsed molecular beam in a MW cavity: the low rotational temperature prevailing in the molecular beam, typically $\approx 2 - 3\,\text{K}$, and the superior sensitivity compared to Stark-modulation are favourable conditions to detect pure rotational transitions in the ground torsional state. Based on the analogy to the anhydrides mentioned above the frame of acetanhydride was initially assumed to be planar, although as a result of a structure determination by electron diffraction[5] the frame is stated to be non-planar with C_2 symmetry.

The expected and observed MW spectra of acetanhydride between 8 and 26 GHz, and the conclusions concerning the conformation in the molecular beam and the barriers of internal rotation will be presented.

---

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383

Q39

SPECTROMETRIC AND PHOTOACOUSTIC COMBINED
SPECTROMETER

M.R. DE BACKER*, V. ZENINARI*, D. COURTOIS*,

Yu. N. PONOMAREV**, O.V. TIKHOMIROVA**,

B.A. TIKHOMIROV**

*G.S.M.A., U.A. CNRS D 1434, Faculté des Sciences

BP 347 - 51062 REIMS Cédex - France

** Laboratory of Absorption Atmosheric Spectroscopy, Institute of

Atmospheric Optics of SBRAS, Tomsk 634055 - Russia

High resolution diode laser spectrophotometry in the 10 μm region is
successfully applied to record ozone absorption spectra. Continuous and
precise control of ozone concentration is required for high precision
measurements of ozone molecular parameters. To cover the wide dynamic
range of the different absorption lines, cells with different optical pathlength
have to be used. In this paper, the recorded spectra with the combined
spectrometer are presented. The spectrometer of the Reims GSMA
Laboratory (France) uses a photoacoustic cell designed in the Institute of
Atmospheric Optics of SBRAS. The scheme and the characteristics of the
spectrometer are detailed. This spectrometer allows to simultaneously record
ozone absorption spectra by spectrophotometric and photoacoustic methods.
Absorption spectra of ozone in mixture with Ar have been recorded in the
1048 cm^{-1} spectral range with a $Pb_{1-x} Sn_x$ Se diode laser. The total
pressure is 20 Torr and the various O_3 partial pressures range from 0.04 to
1.1 Torr. The spectra obtained by the two methods show good agreement. A
procedure is proposed to control the O_3 concentration fluctuation by
recording a photoacoustic signal. This signal can be obtained at a fixed laser
wavelength : CO_2 laser in the v_3 vibrational band or He-Ne laser in the
Chappuis electronic band. The transmission spectra can be recorded
simultaneously with the diode laser. The two optical beams are modulated at
different frequencies.

Q40

WAVENUMBER MEASUREMENTS OF MOLECULAR TRANSITIONS IN THE 1.2 μm - 1.5 μm RANGE BY FOURIER TRANSFORM SPECTROSCOPY

Q. Kou, Ph. Cousson, R. Farrenq, A. Ubelmann, G. Guelachvili
Laboratoire de Physique Moléculaire et Applications, CNRS
Université de Paris-Sud, Bât 350, 91405 Orsay, France

Accurate wavenumber scale calibration in the 1.2 μm - 1.5 μm region has a growing importance in the optical communication technology using semiconductor laser diodes. Absolute standards are needed for the frequency stabilisation of the laser emission of those diodes to improve the efficiency of the optical transmission process. However, the wavenumber standards are dramatically missing in the region over 5000 cm^{-1}, as shown in the poster (1) presented in this colloquium.

High resolution Fourier absorption measurements of C_2H_2, NH_3, CO_2 and H_2O in the 1.2 μm - 1.5 μm region are presented. The spectra are recorded at Doppler-limited resolution with an average signal to noise ratio better than 1000. The wavenumbers of the molecular transitions are measured against the rovibrational lines of the 3-0 band of CO calculated from an improved set of Dunham coefficients[2]. The absolute uncertainty of the measurements is estimated to 3 x 10^{-4} cm^{-1}.

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Q41

PHOTON ECHO STUDY OF MOLECULAR COLLISIONS

L.S.Vasilenko, N.N.Rubtsova, and E.B.Hvorostov

Institute of Semiconductor Physics, RAS,

prosp. acad. Lavrentyev, 13,

Novosibirsk 630090, Russia

Photon echo created by exciting pulses of CO_2 laser radiation (line 10P(18)) in gase SF_6 (P(33) A_2^1 rotational transition of $0 \rightarrow 1$ ν_3 vibrational mode) and its mixtures with buffers He and Xe was studied in a wide range of intensities and areas of exciting pulses.

It is shown experimentally, that both exciting pulses small areas and low intensities are necessary conditions, providing the main advantage of the method — the possibility to study collisions of particles ensemble with definite longitudinal velocities v_s. These conditions warrant high accuracy of Γ (v_s) measurements[1], providing with data about intermolecular potential steepness. Small areas and low intensities requirements are especially important for heavy perturber mixtures (SF_6+Xe), where intensity dependent echo decay kinetics was registrated. The last one is explained by simultaneous dependence of homogeneous broadening Γ (v_s) and exciting pulses areas Θ (v_s) on relative velocities v_s.

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Q42

COHERENT TRANSIENT SPECTROSCOPY
OF HIGH RESOLUTION IN GAS

L.S.Vasilenko, N.N.Rubtsova, and E.B.Hvorostov

Institute of Semiconductor Physics, RAS,

prosp. acad. Lavrentyev, 13,

Novosibirsk 630090, Russia

Coherent radiation in time separated fields (CRTSF) is the Doppler free technique of high resolution spectroscopy [1], which is advantageous in S/N ratio as compared to saturated absorption spectroscopy (SAS). CRTSF gives rise to overcome transit-time effect, which is the limiting factor of SAS.

Experiments on coherent transients in molecular gases SF_6 and $^{15}NH_3$, performed in essential transit time conditions, have demonstrated[2] ability of coherent transients to select slowly moving particles in both longitudinal and transverse (relative light propagation) directions. Effective temperatures of these molecular ensembles of about $1°K$ is reached [2]. Perspectives for high resolution spectroscopy of slowly moving particles by coherent transients is confirmed.

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Thes. 12-th Intern. Conf. on Spectral Line Shapes,
13-17 June 1994, Toronto, Canada, p. PC-19

R1

Potential Energy Surfaces from the Spectroscopy of Van der Waals Complexes: closed-shell and open-shell systems

Jeremy M. Hutson

Department of Chemistry, University of Durham, Durham, DH1 3LE, England

For simple closed-shell Van der Waals complexes, such as Ar–HF [1] and Ar–HCl [2], high-resolution microwave, far-infrared and mid-infrared spectra have been inverted to give very accurate intermolecular potential energy surfaces that are a function of the intermolecular distance R, the intermolecular angle θ and the diatom bond length r or mass-reduced vibrational quantum number $\eta = (v+\frac{1}{2})/\sqrt{\mu}$. These are the most accurate intermolecular potentials available for any system: they perform well in calculations of other spectroscopic bands [3] and of collisional properties such as pressure broadening [4], and have been of great value in testing new *ab initio* methods. Analogous potentials have also been developed for a few heavier or more complicated closed-shell systems [5], such as Ar–CO$_2$, Ar–H$_2$O, Ar–NH$_3$, HCl–HCl and HF–HF, although for these systems the experimental results are less complete and the potentials are not so fully determined.

High-resolution spectra of open-shell complexes have now started to appear, and it should eventually be possible to use them to determine potential energy surfaces of high quality. For these systems, much of the spectroscopy has involved visible or UV bands of the open-shell monomer, and thus probes excited state potentials as well as (and often better than) ground-state potentials. For example, the high-resolution UV spectra of Ar–OH have been used to determine potential surfaces for Ar interacting with OH $(A^2\Sigma)$ [6], while stimulated-emission pumping (SEP) and microwave spectra have been used to determine potential energy surfaces for Ar–OH $(X^2\Pi)$ [7]. For the ground state, in particular, high-resolution far-infrared or near-infrared spectra are really needed before potential surfaces of a quality comparable to those for Ar–HF etc. can be determined.

There has also been a considerable amount of *ab initio* work [8] aimed at calculating potential energy surfaces for complexes containing open-shell molecules and using them to calculate spectra. This work is somewhat different in spirit from our work on potential fitting, but is nevertheless of great value.

A very interesting emerging area is the spectroscopy of systems containing open-shell atoms. Complexes such as Cl–HCl might be formed

in molecular beams, and their spectroscopy would probe the entrance and exit channels of important prototype chemical reactions such as
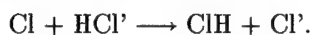
$$Cl + HCl' \longrightarrow ClH + Cl'.$$

We have developed models of the potential energy surfaces for systems containing atoms in P states [9], and have carried out detailed calculations for the specific case of Cl–HCl [10]. We find that the Cl–HCl complex is quite strongly bound (275 cm^{-1}), and has strong far-infrared bending bands predicted around 55 and 78 cm^{-1}. The unusually strong binding occurs because the Cl atom in its $^2P_{3/2}$ state has an electric quadrupole moment, so that there is a strong electrostatic attraction. The observation of spectra of this or similar complexes will provide a fascinating new window on chemically reactive processes.

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R2

HIGHLY EXCITED VIBRATIONAL STATES OF SMALL
POLYATOMIC MOLECULES

Lauri Halonen

Laboratory of Physical Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1),

FIN-00014 University of Helsinki, Finland

Highly excited vibrational states of small polyatomic molecules have been investigated with photoacoustic technique where the sample cell is placed inside a titanium:sapphire/dye ring laser cavity. Doppler limited overtone spectra have been obtained for HCCH, HCCF, HCCCl, HCCBr, HCCI, SbH_3, and SnH_4. The rotational structure of the spectra in different molecules shows varying degree of complexity depending on the importance of Fermi resonance type interactions between different vibrational degrees of freedom. In practice only in the case of SnH_4 the simple local mode model with isolated hydrogen stretching overtones is valid.

Theoretical models for vibrational and rovibrational states have been developed. These include both local mode-Fermi resonance models formulated in terms of curvilinear internal valence coordinates and vibration-rotation Hamiltonians for rotational levels of excited vibrational states in near local mode molecules. Experimental data have been used to determine Born-Oppenheimer potential energy surfaces of some of the molecules studied.

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